

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 164 581 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
19.12.2001 Bulletin 2001/51

(51) Int Cl.7: **G11B 5/706, C01G 49/06**

(21) Application number: **01305101.6**

(22) Date of filing: **12.06.2001**

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR**
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **13.06.2000 JP 2000177377**

(71) Applicant: **Toda Kogyo Corporation
Hiroshima-shi, Hiroshima-ken (JP)**

(72) Inventors:
• **Okinaka, Kenji**
Ube-shi, Yamaguchi-ken (JP)
• **Uegami, Masayuki**
Onoda-shi, Yamaguchi-ken (JP)

(74) Representative: **Woods, Geoffrey Corlett
J.A. KEMP & CO., Gray's Inn, 14 South Square
London WC1R 5JJ (GB)**

(54) **Spindle-shaped goethite particles, spindle-shaped hematite particles, spindle-shaped magnetic metal particles containing iron as main component and processes for producing the same**

(57) The present invention relates to spindle-shaped goethite particles which have an average major axial diameter of from 0.05 to 0.18 μm , an aspect ratio of more than 6:1 and less than 10:1 and a size distribution (standard deviation/average major axial diameter) of not more than 0.20; which contain not less than 0.5

and less than 6 atm% of Co based on the total amount of Fe, and more than 10 and less than 20 atm% of Al based on the total amount of Fe; and which have an atomic ratio of Al to Co of more than 2:1 and not more than 4:1. The particles of the invention may be used in a magnetic recording layer of a magnetic recording medium.

EP 1 164 581 A2

BEST AVAILABLE COPY

Description

[0001] The present invention relates to spindle-shaped goethite particles, spindle-shaped hematite particles, spindle-shaped magnetic metal particles containing iron as a main component, and processes for producing the respective particles. More particularly, the present invention relates to spindle-shaped goethite particles having an average major axial diameter of 0.05 to 0.18 μm , spindle-shaped hematite particles having an average major axial diameter of 0.05 to 0.17 μm , spindle-shaped magnetic metal particles containing iron as a main component, which exhibit an adequate coercive force, good dispersibility, good oxidation stability and excellent coercive force distribution notwithstanding the average major axial diameter thereof is as small as 0.05 to 0.15 μm , and processes for producing the respective particles.

[0002] In recent years, recording-time prolongation, miniaturization and lightening of audio, video or computer magnetic recording and reproducing apparatuses for various magnetic recording media such as digital audio tapes (DAT) for people's livelihood use, 8-mm video tapes, Hi-8 tapes, VTR tapes for business use, computer tapes or discs thereof have proceeded more rapidly. In particular, VTRs (video tape recorders) are now widespread, so that there have been intensely developed VTRs aiming at the transfer of analog recording types into digital ones in addition to the above recording-time prolongation, miniaturization and lightening thereof. On the other hand, with such recent tendencies, the magnetic recording media have been required to have high image quality and high output characteristics, especially high frequency characteristics. To meet these requirements, it is necessary to reduce noise due to the magnetic recording media themselves and enhance residual magnetic flux density, coercive force, dispersibility, filling property and tape-surface smoothness thereof. Therefore, it has been further required to improve S/N ratio of the magnetic recording media.

[0003] These properties of the magnetic recording media have a close relation to magnetic particles used therein. In recent years, magnetic metal particles containing iron as a main component have been noticed because such particles can show a higher coercive force and a larger saturation magnetization as compared to those of conventional magnetic iron oxide particles, and have been already used as magnetic particles for magnetic recording media such as DAT, 8-mm video tapes, Hi-8 tapes, video tapes for business use, computer tapes or discs. The magnetic metal particles containing iron as a main component conventionally used in DAT, 8-mm video tapes, Hi-8 tapes or the like have been required to be further improved in output characteristics and weather resistance. In addition, the magnetic metal particles containing iron as a main component must fulfill applicability to existing format and good economy at the same time. Therefore, it has been strongly required to provide magnetic metal particles containing iron as a main component capable of satisfying the above requirements while minimizing amounts of various metals added thereto.

[0004] Various properties of magnetic recording media are detailed below.

[0005] In order to obtain high image quality in video magnetic recording media, it has been required to enhance S/N ratio and video frequency characteristics thereof. For this reason, it is important to improve a surface smoothness of the magnetic recording media. For improving the surface smoothness, it is also required to improve a dispersibility of magnetic particles in coating composition as well as orientation and filling properties thereof in coating film. In addition, in order to enhance the video frequency characteristics, the magnetic recording media have been required to exhibit not only a high coercive force and a large residual magnetic flux density, but also an excellent S.F.D. (Switching Field Distribution), i.e., a small coercive force distribution. Further, the magnetic recording media are required to show good running property upon repeated use, good still property as well as high recording reliability even when used under severe environmental conditions, i.e., high durability.

[0006] As to the magnetic metal particles containing iron as a main component for magnetic recording media capable of satisfying the above various properties, those having a larger particle size are preferable from the standpoint of improvement in dispersibility and oxidation stability, while those having a smaller particle size are preferable from the standpoint of improvement in surface smoothness and reduction in noise. Thus, the smaller the particle size of the magnetic metal particles containing iron as a main component, the poorer the dispersibility and oxidation stability thereof. Also, when the particle size becomes smaller, the coercive force is usually increased. Therefore, it is necessary to appropriately control the particle size for attaining aimed magnetic properties. Further, it is preferable to incorporate a large amount of cobalt into the magnetic metal particles containing iron as a main component in the consideration of chemical composition thereof since as well known, which cobalt forms a solid solution with iron and contributes to improvement in oxidation stability. However, the use of a large amount of expensive cobalt is disadvantageous from economical viewpoint. Consequently, it has been demanded to provide magnetic metal particles containing iron as a main component exhibiting an adequate coercive force as well as excellent dispersibility and oxidation stability in spite of lessening contents of expensive metal elements such as cobalt and reducing the particle size.

[0007] As known in the arts, the magnetic metal particles containing iron as a main component are produced by heat-treating goethite particles, hematite particles obtained by heat-dehydrating the goethite particles, or particles obtained by incorporating different metal elements into the above goethite or hematite particles as starting material, if required, in a non-reducing atmosphere; and then heat-reducing the resultant particles in a reducing atmosphere. In

this case, it is required that the magnetic metal particles containing iron as a main component still maintain shape and size of the goethite particles as starting material by appropriately controlling the shape and size of the goethite particles or by preventing heat fusion between particles upon heat-treatments such as heat-dehydration and heat-reduction, or deformation and breakage of each particle.

[0008] The starting goethite particles are classified into two kinds of goethite particles in accordance with configurations thereof, i.e., acicular goethite particles produced mainly from alkali hydroxide and spindle-shaped goethite particles produced mainly from alkali carbonate. The acicular goethite particles usually tend to have a large aspect ratio, but tend to be deteriorated in particle size distribution and become large in size as compared to spindle-shaped goethite particles. The particle size distribution is an index of uniformity of primary particles, and, therefore, has a close relationship with coercive force distribution and oxidation stability of the magnetic metal particles containing iron as a main component. Consequently, spindle-shaped goethite particles having an excellent particle size distribution are preferably used as the starting materials of the magnetic metal particles containing iron as a main component.

[0009] Under these circumstances, as magnetic metal particles containing iron as a main component used for audio or video magnetic recording media such as digital audio tapes (DAT) for people's livelihood use, 8-mm video tapes and Hi-8 tapes, there have been demanded such magnetic metal particles containing iron as a main component having an adequate coercive force of 111.4 to 143.2 kA/m (1,400 to 1,800 Oe) as well as good dispersibility and oxidation stability even when the content of expensive elements such as cobalt is lessened and the particle size is minimized in order to further improve the properties of the magnetic metal particles containing iron as a main component and pursue better economy.

[0010] As to compositions of magnetic metal particles containing iron as a main component for improving various properties thereof, there are known those specified in, e.g., Japanese Patent Application Laid-Open (KOKAI) Nos. 7-210856, 8-279142, 9-293233, 9-295814, 10-69629, 10-245233, 10-275326, 10-334455, 10-334457, 11-11951, 11-130439, 11-251122 or the like.

[0011] At present, it has been strongly required to provide spindle-shaped magnetic metal particles containing iron as a main component, which can exhibit an adequate coercive force of 111.4 to 143.2 kA/m (1,400 to 1,800 Oe), good dispersibility, good oxidation stability and excellent coercive force distribution in spite of fine particles, especially notwithstanding the average major axial diameter thereof is as small as 0.05 to 0.15 μm . However, such spindle-shaped magnetic metal particles containing iron as a main component cannot be obtained yet.

[0012] Namely, in the above-described KOKAIs, although the contents of Co, Al and rare earth element based on whole Fe are specified, there are no descriptions concerning relationship between the respective elements. These conventional despite fail to satisfy the above requirement of exhibiting an adequate coercive force, excellent dispersibility and excellent oxidation stability at the same time in spite of fine particles.

[0013] As a result of the present inventors' earnest studies for solving the above problems, it has been found that in the process for producing spindle-shaped goethite particles, comprising reacting an aqueous ferrous salt solution with a mixed aqueous alkali solution of an aqueous alkali carbonate solution and an aqueous alkali hydroxide solution; aging the resultant water suspension containing a ferrous-containing precipitate in a non-reducing atmosphere; passing an oxygen-containing gas through the water suspension to conduct an oxidation reaction thereof, thereby producing spindle-shaped goethite seed crystal particles; passing an oxygen-containing gas through the water suspension containing the spindle-shaped goethite seed crystal particles and the ferrous-containing precipitate to conduct an oxidation reaction thereof, thereby growing a goethite layer on the surface of each spindle-shaped goethite seed crystal particle, so that spindle-shaped goethite particles are obtained; and heat-treating the resultant spindle-shaped goethite particles in a non-reducing atmosphere; and then heat-reducing the obtained particles in a reducing atmosphere,

by adding a Co compound in an amount of from 0.5 to less than 6 atm% (calculated as Co) based on whole Fe, to the water suspension containing the ferrous-containing precipitate during aging but prior to the elapse of half a period of the whole aging time before initiation of the oxidation reaction; conducting the oxidation reaction for producing the spindle-shaped goethite seed crystal particles, such that 40 to 50% of whole Fe^{2+} is oxidized; adding an Al compound in an amount of from more than 10 to less than 20 atm% (calculated as Al) based on whole Fe, to the water suspension containing the spindle-shaped goethite seed crystal particles and ferrous-containing precipitate before initiation of the oxidation reaction,

the thus obtained spindle-shaped magnetic metal particles containing iron as a main component can exhibit not only adequate coercive force, good dispersibility and good oxidation stability, but also excellent coercive force distribution notwithstanding the average major axial diameter thereof is as small as 0.05 to 0.15 μm . The present invention has been attained on the basis of this finding.

[0014] An object of the present invention is to provide fine spindle-shaped magnetic metal particles containing iron as a main component, which can exhibit not only adequate coercive force, good dispersibility and good oxidation stability, but also excellent coercive force distribution in spite of the average major axial diameter thereof of as small as 0.05 to 0.15 μm .

[0015] Another object of the present invention is to provide fine spindle-shaped hematite particles having an average

major axial diameter of 0.05 to 0.17 μm and a specific crystallite size ratio, which are suitably used as a starting material of the fine spindle-shaped magnetic metal particles containing iron as a main component which can exhibit not only adequate coercive force, good dispersibility and good oxidation stability, but also excellent coercive force distribution.

[0016] Still another object of the present invention is to provide fine spindle-shaped goethite particles having an average major axial diameter of 0.05 to 0.18 μm , a relatively small aspect ratio and a specific crystallite size ratio, which are suitably used as a starting material of the fine spindle-shaped magnetic metal particles containing iron as a main component which can exhibit not only adequate coercive force, good dispersibility and good oxidation stability, but also excellent coercive force distribution.

[0017] To accomplish the aim, in a first aspect of the present invention, there are provided spindle-shaped goethite particles having an average minor axial diameter of 0.05 to 0.18 μm , an aspect ratio of from more than 6:1 to less than 10:1, a size distribution (standard deviation/average major axial diameter) of not more than 0.20, a Co content of from 0.5 to less than 6 atm% based on whole Fe; an Al content of from more than 10 to less than 20 atm% based on whole Fe, and an atomic ratio of Al to Co of from more than 2 to 4.

[0018] In a second aspect of the present invention, there are provided spindle-shaped goethite particles having an average major axial diameter of 0.05 to 0.18 μm , an aspect ratio of from more than 6:1 to less than 10:1, a size distribution (standard deviation/average major axial diameter) of not more than 0.20, a Co content of from 0.5 to less than 5 atm% based on whole Fe; an Al content of from 10.5 to less than 18 atm% based on whole Fe, an atomic ratio of Al to Co of from 2.10 to 3.90, a crystallite size D_{020} of 150 to 250 \AA , a crystallite size D_{110} of 80 to 120 \AA and a crystallite size ratio of D_{020}/D_{110} of 1.8 to 2.4.

[0019] In a third aspect of the present invention, there are provided spindle-shaped hematite particles having an average major axial diameter of 0.05 to 0.17 μm , an aspect ratio of from more than 6:1 to less than 10:1, a size distribution (standard deviation/average major axial diameter) of not more than 0.22, a crystallite size D_{104} of 100 to 140 \AA , a Co content of from 0.5 to less than 6 atm% based on whole Fe; an Al content of from more than 10 to less than 20 atm% based on whole Fe, a rare earth element content of from 1.5 to 5 atm% based on whole Fe, and an atomic ratio of Al to Co of from more than 2 to 4.

[0020] In a fourth aspect of the present invention, there are provided spindle-shaped hematite particles having an average major axial diameter of 0.05 to 0.17 μm , an aspect ratio of from more than 6:1 to less than 10:1, a size distribution (standard deviation/average major axial diameter) of not more than 0.22, a crystallite size D_{104} of 100 to 140 \AA , a Co content of from 0.5 to less than 5 atm% based on whole Fe; an Al content of from 10.5 to less than 18 atm% based on whole Fe, a rare earth element content of from 2.0 to 4.8 atm% based on whole Fe, an atomic ratio of Al to Co of from 2.10 to 3.90, a crystallite size D_{110} of 200 to 300 \AA , and a crystallite size ratio of D_{020}/D_{110} of 2.0 to 4.0.

[0021] In a fifth aspect of the present invention, there are provided spindle-shaped magnetic metal particles containing iron as a main component, having an average major axial diameter of 0.05 to 0.15 μm , an aspect ratio of from 5:1 to 9:1, a size distribution (standard deviation/average major axial diameter) of not more than 0.30, a crystallite size D_{110} of 130 to 160 \AA , a Co content of from 0.5 to less than 6 atm% based on whole Fe, an Al content of from more than 10 to less than 20 atm% based on whole Fe, a rare earth element content of from 1.5 to 5 atm% based on whole Fe, an atomic ratio of Al to Co of from more than 2 to 4, a coercive force of 111.4 to 143.2 kA/m, an oxidation stability of saturation magnetization (Δs) of not more than 10%, and an ignition temperature of not less than 130°C.

[0022] In a sixth aspect of the present invention, there are provided spindle-shaped magnetic metal particles containing iron as a main component, having an average major axial diameter of 0.05 to 0.15 μm , an aspect ratio of from 5:1 to 9:1, a size distribution (standard deviation/average major axial diameter) of not more than 0.30, a crystallite size D_{110} of 130 to 160 \AA , a Co content of from 0.5 to less than 5 atm% based on whole Fe; an Al content of from 10.5 to less than 18 atm% based on whole Fe, a rare earth element content of from 2.0 to 4.8 atm% based on whole Fe, an atomic ratio of Al to Co of from 2.10 to 3.90, a coercive force of 111.4 to 143.2 kA/m, an oxidation stability of saturation magnetization (Δs) of not more than 10%, and an ignition temperature of not less than 130°C.

[0023] In a seventh aspect of the present invention, there is provided a process for producing the spindle-shaped goethite particles, which process comprises:

aging a water suspension containing a ferrous-containing precipitate produced by reacting a mixed aqueous alkali solution comprising an aqueous alkali carbonate solution and an aqueous alkali hydroxide solution with an aqueous ferrous salt solution in a non-oxidative atmosphere;

conducting an oxidation reaction of the water suspension by passing an oxygen-containing gas therethrough, thereby producing spindle-shaped goethite seed crystal particles,

upon the production of the seed crystal particles, a Co compound being added in an amount of from 0.5 to less than 6 atm%, calculated as Co, based on whole Fe, to the water suspension containing the ferrous-containing precipitate during aging thereof but prior to the elapse of half a period of the whole aging time before initiation of the oxidation reaction, and the oxidation reaction being conducted such that 40 to 50% of whole Fe^{2+} is oxidized;

and

after adding an Al compound in an amount of from more than 10 to less than 20 atm%, calculated as Al, based on a whole Fe, to the water suspension containing both the ferrous-containing precipitate and the spindle-shaped goethite seed crystal particles, passing again an oxygen-containing gas through the resultant water suspension so as to conduct an oxidation reaction thereof, thereby growing a goethite layer on the surface of each seed crystal particle.

[0024] In an eighth aspect of the present invention, there is provided a process for producing the spindle-shaped hematite particles, which process comprises:

aging a water suspension containing a ferrous-containing precipitate produced by reacting a mixed aqueous alkali solution comprising an aqueous alkali carbonate solution and an aqueous alkali hydroxide solution with an aqueous ferrous salt solution in a non-oxidative atmosphere;

conducting an oxidation reaction of the water suspension by passing an oxygen-containing gas therethrough, thereby producing spindle-shaped goethite seed crystal particles,

upon the production of the seed crystal particles, a Co compound being added in an amount of from 0.5 to less than 6 atm%, calculated as Co, based on whole Fe, to the water suspension containing the ferrous-containing precipitate during aging thereof but prior to the elapse of half a period of the whole aging time before initiation of the oxidation reaction, and the oxidation reaction being conducted such that 40 to 50% of whole Fe^{2+} is oxidized; after adding an Al compound in an amount of from more than 10 to less than 20 atm%, calculated as Al, based on a whole Fe, to the water suspension containing both the ferrous-containing precipitate and the spindle-shaped goethite seed crystal particles, passing again an oxygen-containing gas through the resultant water suspension so as to conduct an oxidation reaction thereof, thereby growing a goethite layer on the surface of each seed crystal particle;

treating the spindle-shaped goethite particles obtained with an anti-sintering agent containing a rare earth compound in an amount of 1.5 to 5 atm%, calculated as a rare earth element, based on whole Fe; and heat-treating the thus treated spindle-shaped goethite particles at a temperature of 650 to 800°C in a non-reducing atmosphere.

[0025] In a ninth aspect of the present invention, there is provided a process for producing the spindle-shaped magnetic metal particles containing iron as a main component, which process comprises:

aging a water suspension containing a ferrous-containing precipitate produced by reacting a mixed aqueous alkali solution comprising an aqueous alkali carbonate solution and an aqueous alkali hydroxide solution with an aqueous ferrous salt solution in a non-oxidative atmosphere;

conducting an oxidation reaction of the water suspension by passing an oxygen-containing gas therethrough, thereby producing spindle-shaped goethite seed crystal particles,

upon the production of the seed crystal particles, a Co compound being added in an amount of from 0.5 to less than 6 atm%, calculated as Co, based on whole Fe, to the water suspension containing the ferrous-containing precipitate during aging thereof but prior to the elapse of half a period of the whole aging time before initiation of the oxidation reaction, and the oxidation reaction being conducted such that 40 to 50% of whole Fe^{2+} is oxidized; after adding an Al compound in an amount of from more than 10 to less than 20 atm%, calculated as Al, based on a whole Fe, to the water suspension containing both the ferrous-containing precipitate and the spindle-shaped goethite seed crystal particles, passing again an oxygen-containing gas through the resultant water suspension so as to conduct an oxidation reaction thereof, thereby growing a goethite layer on the surface of each seed crystal particle;

treating the spindle-shaped goethite particles obtained with an anti-sintering agent containing a rare earth compound in an amount of 1.5 to 5 atm%, calculated as a rare earth element, based on whole Fe;

heat-treating the thus treated spindle-shaped goethite particles at a temperature of 650 to 800°C in a non-reducing atmosphere;

heat-reducing the spindle-shaped hematite particles obtained at 400 to 700°C in a reducing atmosphere.

[0026] In a tenth aspect of the present invention, there is provided a magnetic recording medium comprising a non-magnetic substrate and a magnetic recording layer formed on the non-magnetic substrate comprising a binder resin and spindle-shaped magnetic metal particles containing iron as a main component, which have an average major axial diameter of 0.05 to 0.15 μm , an aspect ratio of 5:1 to 9:1, a size distribution (standard deviation/average major axial diameter) of not more than 0.30, a crystallite size D_{110} of 130 to 160 Å, a Co content of from 0.5 to less than 6 atm% based on whole Fe; an Al content of from more than 10 to less than 20 atm% based on whole Fe, a rare earth element

content of 1.5 to 5 atm% based on whole Fe, an atomic ratio of Al to Co of from more than 2 to 4, a coercive force of 111.4 to 143.2 kA/m, an oxidation stability of saturation magnetization ($\Delta\sigma_s$) of not more than 10%, and an ignition temperature of not less than 130°C.

[0027] In the accompanying drawings:

[0028] Fig. 1 is a transmission electron micrograph (x30,000) showing a shape of spindle-shaped goethite particle obtained in Example 1.

[0029] Fig. 2 is a transmission electron micrograph (x30,000) showing a shape of spindle-shaped hematite particle obtained in Example 1.

[0030] Fig. 3 is a transmission electron micrograph (x30,000) showing a shape of spindle-shaped magnetic metal particle obtained in Example 1.

[0031] First, the spindle-shaped goethite particles of the present invention are described below.

[0032] The spindle-shaped goethite particles of the present invention have a cobalt content of usually from 0.5 to less than 6 atm%, preferably from 0.5 to less than 5 atm% based on whole Fe contained in the spindle-shaped goethite particles, an aluminum content of usually from more than 10 to less than 20 atm%, preferably from 10.5 to 18 atm% based on whole Fe contained in the spindle-shaped goethite particles, and an atomic ratio of Al to Co of usually from more than 2:1 to 4:1, preferably from 2.10:1 to 3.90:1.

[0033] When the Co content of the spindle-shaped goethite particles is less than 0.5 atm%, the magnetic metal particles containing iron as a main component obtained therefrom falls to show improved magnetic properties. When the Co content is not less than 6 atm%, it is difficult to adequately control the particle size, and the use of such a large amount of Co is economically disadvantageous. When the Al content is not more than 10 atm%, although the anti-sintering effect is attained, the coercive force of the obtained magnetic metal particles containing iron as a main component, especially those having a small particle size, becomes too large, thereby failing to adequately control the coercive force. When the Al content is not less than 20 atm%, particles other than goethite particles tend to be produced, so that the magnetic properties, especially saturation magnetization, of the obtained magnetic metal particles containing iron as a main component are deteriorated.

[0034] When the atomic ratio of Al to Co of the spindle-shaped goethite particles is not more than 2:1, it is difficult to adequately control the coercive force of the magnetic metal particles containing iron as a main component obtained therefrom. When the atomic ratio of Al to Co is more than 4, the crystal growth upon heat-reduction is inhibited, so that the saturation magnetization and oxidation stability of the obtained magnetic metal particles containing iron as a main component tend to be deteriorated.

[0035] The spindle-shaped goethite particles of the present invention are of a spindle shape, and have an average major axial diameter of usually 0.05 to 0.18 μm , preferably 0.009 to 0.18 μm ; a size distribution (standard deviation/average major axial diameter) of usually not more than 0.20, preferably 0.10 to 0.18; and an aspect ratio of usually from more than 6:1 to less than 10:1, preferably 6:1 to 9:1.

[0036] When the average major axial diameter of the spindle-shaped goethite particles is less than 0.05 μm , the magnetic metal particles containing iron as a main component obtained therefrom have a too small particle size which is close to the particle size exhibiting a superparamagnetism, so that the saturation magnetization and coercive force of the magnetic metal particles containing iron as a main component, the dispersibility in coating composition containing the magnetic metal particles containing iron as a main component, and the oxidation stability of the magnetic metal particles containing iron as a main component tend to be deteriorated. When the average major axial diameter of the spindle-shaped goethite particles is more than 0.18 μm , it is difficult to obtain the magnetic metal particles containing iron as a main component having the aimed coercive force. Further, the coating film containing the magnetic metal particles containing iron as a main component tends to be deteriorated in surface smoothness due to the large particle size, thereby failing to improve the output characteristics thereof.

[0037] It is preferred that the size distribution of the spindle-shaped goethite particles of the present invention is as small as possible. Although the lower limit of the size distribution of the spindle-shaped goethite particles is not particularly restricted, in the consideration of industrial productivity, the size distribution is more preferably about 0.08 to about 0.12. When the size distribution of the spindle-shaped goethite particles is more than 0.20, the magnetic metal particles containing iron as a main component obtained therefrom tend to be deteriorated in oxidation stability, thereby failing to achieve a high density recording performance of magnetic recording media. When the aspect ratio of the spindle-shaped goethite particles is less than 6:1, the aimed coercive force cannot be obtained. When the aspect ratio is not less than 10:1, the obtained magnetic metal particles containing iron as a main component exhibit a too high coercive force or are deteriorated in oxidation stability.

[0038] In addition, the spindle-shaped goethite particles of the present invention have a BET specific surface area of usually 130 to 200 m^2/g , preferably 150 to 200 m^2/g . When the BET specific surface area is less than 100 m^2/g , the obtained spindle-shaped goethite particles are relatively large in size, so that the magnetic metal particles containing iron as a main component obtained therefrom tend to fail to exhibit the aimed coercive force. When the BET specific surface area is more than 200 m^2/g , the coercive force of the spindle-shaped magnetic metal particles containing iron

as a main component becomes so high beyond required level, resulting in deteriorated oxidation stability.

[0039] The spindle-shaped goethite particles of the present invention have a crystallite size D_{020} of preferably 150 to 250 Å, more preferably 170 to 230 Å; a crystallite size D_{110} of preferably 80 to 120 Å, more preferably 90 to 110 Å; and a crystallite size ratio of D_{020}/D_{110} of preferably 1.8 to 2.4, more preferably 1.8 to 2.2. When the crystallite size ratio of D_{020}/D_{110} is less than 1.8, the obtained spindle-shaped goethite particles tend to become insufficient in shape-retention property upon heat-dehydration or heat-reduction thereof. As a result, the magnetic metal particles containing iron as a main component obtained therefrom tend to be deteriorated in dispersibility in coating composition as well as coercive force distribution. When the crystallite size ratio of D_{020}/D_{110} of the spindle-shaped goethite particles is more than 2.4, the magnetic metal particles containing iron as a main component obtained therefrom have the aimed particle size, but tend to fail to exhibit the aimed coercive force.

[0040] The spindle-shaped goethite particles of the present invention are each constituted by a seed crystal portion and a surface layer portion. Cobalt is present in both the seed crystal and surface layer portions, while aluminum is present only in the surface layer portion.

[0041] Here, the "seed crystal portion" means a goethite seed crystal particle produced by oxidizing the ferrous salt prior to the addition of the Al compound. More specifically, the seed crystal portion is a portion having a specific weight percentage of Fe determined by the oxidation percentage of Fe^{2+} , preferably a portion extending outwardly from the center of each goethite particle, which portion corresponds to an amount of usually 40 to 50% by weight based on whole Fe contained in the goethite particle.

[0042] The ratio of the crystallite size D_{020} of the spindle-shaped goethite particle according to the present invention to the crystallite size D_{020} of the seed crystal particle thereof [$D_{020}(\text{spindle-shaped goethite particle})/D_{020}(\text{seed crystal particle})$] is preferably 1.05 to 1.20; and the ratio of the crystallite size D_{110} of the spindle-shaped goethite particle according to the present invention to the crystallite size D_{110} of the seed crystal particle thereof [$D_{110}(\text{spindle-shaped goethite particle})/D_{110}(\text{seed crystal particle})$] is preferably 1.02 to 1.10. When the crystallite size ratio of $D_{020}(\text{spindle-shaped goethite particle})/D_{020}(\text{seed crystal particle})$ is more than 1.20 or the crystallite size ratio of $D_{110}(\text{spindle-shaped goethite particle})/D_{110}(\text{seed crystal particle})$ is more than 1.10, the goethite layer constituting the surface layer portion becomes too thick, so that it tends to be difficult to adequately control the shape of each goethite particle. When the crystallite size ratio of $D_{020}(\text{spindle-shaped goethite particle})/D_{020}(\text{seed crystal particle})$ is less than 1.05 or the crystallite size ratio of $D_{110}(\text{spindle-shaped goethite particle})/D_{110}(\text{seed crystal particle})$ is less than 1.02, the goethite layer constituting the surface layer portion becomes too thin, so that the anti-sintering effect tends to be considerably lowered upon the heat-dehydration and heat-reduction treatments.

[0043] The existence amount of Co (Co concentration) contained in the seed crystal portion is preferably 75 to 95, more preferably 80 to 90 based on the total amount of Co (Co concentration) contained in whole spindle-shaped goethite particle of the present invention, assuming that the total amount of Co (Co concentration) is 100. The existence amount of Co (Co concentration) contained in the surface layer portion is preferably 103 to 125, more preferably 106 to 120 based on the total amount of Co (Co concentration) contained in whole spindle-shaped goethite particle of the present invention.

[0044] When the existence amount of Co (Co concentration) contained in the seed crystal portion is less than 75 and the existence amount of Co (Co concentration) contained in the surface layer portion is more than 125, the Co content of the seed crystal portion becomes small, thereby failing to form a Co alloy, while the Co content of the surface layer becomes excessive, thereby failing to exhibit a adequate shape-retention property upon heat-reduction, and further resulting in deteriorated magnetic properties of the obtained magnetic metal particles containing iron as a main component. When the existence amount of Co (Co concentration) contained in the seed crystal portion is more than 95 and the existence amount of Co (Co concentration) contained in the surface layer portion is less than 103, although the Co content of the seed crystal portion is sufficient to form a Co alloy, the amount of Al contained in the surface layer portion becomes too large based on the amount of Co coexisting therein, thereby failing to form a Co alloy in the surface layer portion. As a result, the magnetic metal particles containing iron as a main component obtained from such spindle-shaped goethite particles tend to be deteriorated in magnetic properties as a whole.

[0045] Also, the "surface layer portion" means a goethite layer formed by the crystal growth on the goethite seed crystal particle after the addition of the Al compound during the growth reaction. More specifically, the surface layer portion is a portion extending inwardly from the outermost surface of each goethite particle, which portion corresponds to an amount of usually 50 to 60% by weight based on whole Fe contained in the goethite particle. Aluminum is present only in the surface layer portion. When a too large amount of Al is present in the surface layer portion, the crystal growth within each particle is inhibited. As a result, the magnetic metal particles containing iron as a main component obtained from such spindle-shaped goethite particles tend to fail to exhibit the aimed coercive force.

[0046] Next, the process for producing the spindle-shaped goethite particles according to the present invention is described below.

[0047] The spindle-shaped goethite particles according to the present invention are produced by first forming spindle-shaped goethite seed crystal particles and then growing a goethite layer on the surface of respective goethite seed

crystal particles.

[0048] The spindle-shaped goethite seed crystal particles are obtained as follows. That is, in the production of the spindle-shaped goethite seed crystal particles comprising reacting an aqueous ferrous salt solution with a mixed aqueous alkali solution of an aqueous alkali carbonate solution and an aqueous alkali hydroxide solution; aging the resultant water suspension containing a ferrous-containing precipitate in a non-reducing atmosphere; and then passing an oxygen-containing gas through the water suspension to conduct an oxidation reaction thereof, a Co compound is added in an amount of usually from 0.5 to less than 6 atm%, preferably from 0.5 to less than 5 atm% (calculated as Co) based on whole Fe, to the water suspension containing the ferrous-containing precipitate during aging of the water suspension but prior to the elapse of half a period of the whole aging time before initiation of the oxidation reaction, and then the oxidation reaction for producing the spindle-shaped goethite seed crystal particles is conducted such that usually 40 to 50% of whole Fe^{2+} is oxidized.

[0049] When the Co compound is added after the elapse of half a period of the whole aging time, goethite particles having the aimed particle size and aspect ratio cannot be obtained. In addition, when the oxidation percentage of whole Fe^{2+} upon conducting the oxidation reaction is less than 40% or more than 50%, it is also difficult to obtain goethite particles having the aimed particle size and aspect ratio.

[0050] The aging of the water suspension is conducted at a temperature of preferably 40 to 80°C in a non-oxidative atmosphere. When the aging temperature is less than 40°C, a sufficient aging effect cannot be attained, so that the obtained goethite particles have a small aspect ratio. When the aging temperature is more than 80°C, magnetite particles tend to be produced and mixed in the aimed goethite seed crystal particles. The aging time is usually 30 to 300 minutes. When the aging time is less than 30 minutes or more than 300 minutes, it becomes difficult to obtain particles having the aimed aspect ratio. In order to produce the non-oxidative atmosphere, an inert gas such as nitrogen or a reducing gas such as hydrogen may be passed through a reactor containing the water suspension.

[0051] As the aqueous ferrous salt solution used in the production reaction of the spindle-shaped goethite seed crystal particles, there may be used an aqueous ferrous sulfate solution, an aqueous ferrous chloride solution or the like. These solutions may be used singly or in the form of a mixture of any two or more thereof.

[0052] The mixed aqueous alkali solution used in the production reaction of the spindle-shaped goethite seed crystal particles may be produced by mixing an aqueous alkali carbonate solution with an aqueous alkali hydroxide solution. The mixing percentage of these aqueous solutions (% calculated as normality) is adjusted such that the concentration of the aqueous alkali hydroxide solution is preferably 10 to 40%, more preferably 15 to 35% (calculated as normality). When the concentration of the aqueous alkali hydroxide solution is less than 10%, there is a tendency that goethite particles having the aimed aspect ratio cannot be obtained. When the concentration of the aqueous alkali hydroxide solution is more than 40%, granular magnetite particles tend to be produced and mixed in the aimed spindle-shaped goethite seed crystal particles.

[0053] As the aqueous alkali carbonate solution, there may be used an aqueous sodium carbonate solution, an aqueous potassium carbonate solution, an aqueous ammonium carbonate solution or the like. As the aqueous alkali hydroxide solution, there may be used an aqueous sodium hydroxide solution, an aqueous potassium hydroxide solution or the like. These solutions may be respectively used singly or in the form of a mixture of any two or more thereof.

[0054] The amount of the mixed aqueous alkali solution used is usually 1.3 to 3.5, preferably 1.5 to 2.5 when expressed by the equivalent ratio of alkali contained therein to whole Fe contained in the aqueous ferrous salt solution. When the amount of the mixed aqueous alkali solution used is less than 1.3, magnetite particles tend to be produced and mixed in the aimed spindle-shaped goethite particles. When the amount of the mixed aqueous alkali solution used is more than 3.5, the use of such a large amount of alkali becomes industrially disadvantageous.

[0055] The ferrous ion concentration of the solution obtained by mixing the aqueous ferrous salt solution with the mixed aqueous alkali solution is preferably 0.1 to 1.0 mol/liter, more preferably 0.2 to 0.8 mol/liter. When the ferrous ion concentration is less than 0.1 mol/liter, the yield of the aimed goethite particles is lowered, resulting in industrially disadvantageous process. When the ferrous ion concentration is more than 1.0 mol/liter, the particle size distribution of the obtained particles becomes too broad.

[0056] The pH value of the solution used in the production reaction of the spindle-shaped goethite seed crystal particles is preferably 8.0 to 11.5, more preferably 8.5 to 11.0. When the pH value is less than 8.0, a large amount of acid radicals are contained in the obtained goethite particles. Since the acid radicals cannot be removed by simple washing method, the goethite particles tend to be sintered together when heat-treated to form magnetic metal particles containing iron as a main component. When the pH value is more than 11.5, the obtained magnetic metal particles containing iron as a main component tend to fail to exhibit the aimed coercive force.

[0057] The production of the spindle-shaped goethite seed crystal particles is conducted by the oxidation reaction, i.e., by passing an oxygen-containing gas such as air through the solution.

[0058] The superficial velocity of the oxygen-containing gas is preferably 0.5 to 3.5 cm/s, more preferably 1.0 to 3.0 cm/s. When the superficial velocity is less than 0.5 cm/s, the oxidation velocity is too low, so that granular magnetite particles tend to be produced and mixed in the aimed spindle-shaped seed crystal particles. When the superficial

velocity is more than 3.5 cm/s, the oxidation velocity is too high, so that it becomes difficult to control the particle size as required. Here, the "superficial velocity" means an amount of the oxygen-containing gas passed per unit sectional area (bottom sectional area of a cylindrical reactor where the pore diameter and pore number of a perforated plate are ignored; unit: cm/sec).

[0059] The production reaction of the spindle-shaped goethite seed crystal particles may be sufficiently conducted at a temperature of not more than 80°C. When the reaction temperature is more than 80°C, magnetite particles tend to be produced and mixed in the aimed spindle-shaped goethite particles. The reaction temperature is preferably 45 to 55°C.

[0060] As the Co compound added in the production reaction of the spindle-shaped goethite seed crystal particles, there may be used cobalt sulfate, cobalt chloride, cobalt nitrate or the like. These Co compounds may be used singly or in the form of a mixture of any two or more thereof. The Co compound is added to the water suspension containing the ferrous-containing precipitate during the aging thereof before initiation of the oxidation reaction.

[0061] The amount of the Co compound added is usually from 0.5 to less than 6 atm%, preferably from 0.5 to less than 5 atm% based on whole Fe contained in the spindle-shaped goethite particles as a final product.

[0062] The pH value of the water suspension used in the growth reaction of the goethite layer is usually 8.0 to 11.5, preferably 8.5 to 11.0. When the pH value is less than 8.0, a large amount of acid radicals are contained in the obtained goethite particles. Since such acid radicals cannot be removed by simple washing method, the goethite particles tend to be sintered together when heat-treated to form magnetic metal particles containing iron as a main component. When the pH value is more than 11.5, it tends to be difficult to obtain particles having the aimed particle size distribution.

[0063] The growth of the goethite layer is conducted by the oxidation reaction, i.e., by passing an oxygen-containing gas such as air through the water suspension. The superficial velocity of the oxygen-containing gas used in the growth reaction of the goethite layer is preferably larger than that used in the production reaction of the seed crystal particles. When the superficial velocity used in the growth reaction of the goethite layer is not larger than that used in the production reaction of the seed crystal particles, the viscosity of the water suspension is increased by the addition of Al. As a result, the growth in the minor axial direction is more remarkably accelerated, so that the aspect ratio is decreased, thereby failing to obtain particles having the aimed aspect ratio. However, when the superficial velocity used in the production reaction of the seed crystal particles is not less than 2.0 cm/s, the above requirement is not needed.

[0064] The growth reaction of the goethite layer may be sufficiently conducted at a temperature of usually not more than 80°C at which goethite particles can be produced. When the growth reaction temperature is more than 80°C, magnetite particles tend to be produced and mixed in the aimed goethite particles. The lower limit is 30°C. The growth reaction temperature is preferably 45 to 55°C.

[0065] As the Al compound added in the growth reaction of the goethite layer, there may be used acid salts such as aluminum sulfate, aluminum chloride and aluminum nitrate; and aluminates such as sodium aluminate, potassium aluminate and ammonium aluminate. These Al compounds may be used singly or in the form of a mixture of any two or more thereof.

[0066] In the growth reaction of the goethite layer, the Al compound may be added simultaneously with the oxidation reaction in which the oxygen-containing gas is passed through the water suspension at such a superficial velocity preferably larger than that used in the production reaction of the seed crystal particles. When the addition of the Al compound requires a long period of time, the oxygen-containing gas may be replaced with a nitrogen-containing gas so as not to accelerate the oxidation reaction. Meanwhile, when the addition of Al is prolonged, namely the Al compound is added in separate parts, continuously or intermittently while passing the oxygen-containing gas through the water suspension, it is not possible to sufficiently attain the effects of the present invention.

[0067] The amount of the Al compound added is usually from more than 10 to less than 20 atm% based on whole Fe contained in the spindle-shaped goethite particles as a final product.

[0068] Next, the spindle-shaped hematite particles of the present invention are described below.

[0069] The spindle-shaped hematite particles of the present invention contain Co in an amount of usually from 0.5 to less than 6 atm%, preferably from 0.5 to less than 5 atm% based on whole Fe contained in the spindle-shaped hematite particles; Al in an amount of usually from more than 10 to less than 20 atm%, preferably from 10.5 to 18 atm% based on whole Fe contained in the spindle-shaped hematite particles; a rare earth element in an amount of usually from 1.5 to 5 atm%, preferably from 2.0 to 4.8 atm% based on whole Fe contained in the spindle-shaped hematite particles, and have an atomic ratio of Al to Co of usually from more than 2 to 4, preferably from 2.10 to 3.90. The reasons why the Al and Co contents and the atomic ratio of Al to Co of the spindle-shaped hematite particles are defined to the above ranges, are the same as those described in the production of the goethite particles. When the rare earth element content of the spindle-shaped hematite particles is less than 1.5 atm%, a sufficient anti-sintering effect cannot be obtained. As a result, the magnetic metal particles containing iron as a main component obtained from such hematite particles are deteriorated in size distribution, and further the magnetic coating film produced therefrom is deteriorated in SFD. When the rare earth element content is more than 5 atm%, the saturation magnetization of the obtained magnetic metal particles containing iron as a main component is remarkably deteriorated.

[0070] The spindle-shaped hematite particles of the present invention are of a spindle shape, and have an average major axial diameter of usually 0.05 to 0.17 μm , preferably 0.08 to 0.17 μm ; a size distribution (standard deviation/average major axial diameter) of usually not more than 0.22, preferably 0.10 to 0.21; and an aspect ratio of usually from more than 6:1 to less than 10:1, preferably 6:1 to 9:1.

5 **[0071]** When the average major axial diameter of the spindle-shaped hematite particles is less than 0.05 μm , the magnetic metal particles containing iron as a main component obtained therefrom have a too small particle size which is close to the particle size exhibiting a superparamagnetism, so that the saturation magnetization and coercive force of the magnetic metal particles containing iron as a main component as well as the dispersibility in coating composition containing the magnetic metal particles containing iron as a main component and the oxidation stability of the magnetic
10 metal particles containing iron as a main component tend to be deteriorated. When the average major axial diameter of the spindle-shaped hematite particles is more than 0.17 μm , it is difficult to obtain the magnetic metal particles containing iron as a main component the aimed coercive force. In addition, since the particle size becomes too large, the obtained magnetic coating film containing the magnetic metal particles containing iron as a main component tends to be deteriorated in surface smoothness, resulting in poor output characteristics thereof.

15 **[0072]** It is preferred that the size distribution of the spindle-shaped hematite particles of the present invention is as small as possible. Although the lower limit of the size distribution is not particularly restricted, in the consideration of industrial productivity, the size distribution is more preferably about 0.08 to about 0.12. When the size distribution of the spindle-shaped hematite particles is more than 0.22, the obtained magnetic metal particles containing iron as a main component tends to be deteriorated in oxidation stability, thereby failing to obtain magnetic recording media
20 having a high density recording performance. When the aspect ratio is not more than 6:1, there is a tendency that the obtained magnetic metal particles containing iron as a main component cannot exhibit the aimed coercive force. When the aspect ratio is not less than 10:1, the obtained magnetic metal particles containing iron as a main component tend to exhibit a too high coercive force or be deteriorated in oxidation stability.

25 **[0073]** The spindle-shaped hematite particles of the present invention have a BET specific surface area of preferably 40 to 70 m^2/g , more preferably 40 to 60 m^2/g . When the BET specific surface area is less than 40 m^2/g , the obtained hematite particles having the particle size specified by the present invention are already sintered together upon the heat-treatment and, therefore, tend to be deteriorated in size distribution. As a result, the magnetic metal particles containing iron as a main component obtained from such hematite particles also tend to be deteriorated in size distribution, and further the magnetic coating film produced using the magnetic metal particles containing iron as a main
30 component tend to be deteriorated in SFD. When the BET specific surface area is more than 70 m^2/g , the anti-sintering effect becomes insufficient upon the heat-reduction treatment. As a result, the magnetic metal particles containing iron as a main component obtained from such hematite particles tend to be deteriorated in size distribution, and further the magnetic coating film produced therefrom tend to be deteriorated in SFD.

35 **[0074]** The spindle-shaped hematite particles of the present invention have a crystallite size D_{104} of usually 100 to 140 \AA , preferably 110 to 140 \AA ; a crystallite size D_{110} of usually 200 to 300 \AA , preferably 250 to 300 \AA ; and a crystallite size ratio D_{110}/D_{104} of preferably 2.0 to 4.0, more preferably 2.0 to 3.0. When the crystallite size ratio D_{110}/D_{104} is less than 2.0, excessive crystal growth of particles tends to be caused upon the heat-dehydration treatment. Therefore, in combination with the accelerated growth in the minor axial direction, the obtained particles tend to be deteriorated in particle size distribution. As a result, the magnetic metal particles containing iron as a main component obtained from
40 the hematite particles tend to be lowered in coercive force and deteriorated in dispersibility. When the crystallite size ratio D_{110}/D_{104} of the spindle-shaped hematite particles is more than 4.0, the crystal growth upon the heat-dehydration treatment is insufficient, so that a good shape-retention effect cannot be expected upon the heat-reduction treatment. As a result, the obtained magnetic metal particles containing iron as a main component tend to be deteriorated in coercive force and particle size distribution.

45 **[0075]** The spindle-shaped hematite particles of the present invention are each constituted from a seed crystal portion, an intermediate layer portion and an outermost layer portion. Cobalt is present in both the seed crystal and intermediate layer portions, while aluminum is present only in the intermediate layer portion and the rare earth element is present only in the outermost layer portion.

50 **[0076]** Here, the "seed crystal portion" of each hematite particle is the same as the seed crystal portion of the above goethite particle. The seed crystal portion is preferably a portion extending outwardly from the center of each hematite particle, which corresponds to the portion containing Fe in an amount of usually 40 to 50% by weight based on whole Fe contained in each hematite particle. The intermediate layer portion of each hematite particle is the same as the surface layer portion of the above goethite particle. The intermediate layer portion is preferably a portion extending inwardly from the inner surface of the rare earth element-containing outermost layer up to the outer surface of the seed
55 crystal portion, which corresponds to a portion containing Fe in an amount of usually 50 to 60% by weight based on whole Fe contained in each hematite particle.

[0077] The existence amounts of Co (Co concentration) contained in the seed crystal portion and the intermediate layer portion are the same as those of the seed crystal portion and the surface layer portion of the above goethite

particles. Meanwhile, Co may be present in the outermost layer portion, if required. In this case, Co contained in the outermost layer portion shows different effects from those contained in the seed crystal and intermediate layer portions, i.e., contributes to control of the reducing velocity as a whole or enhance the oxidation stability of the outermost surface, etc. Also, another important role of Co is that Co coexists together with Fe within each particle, thereby directly contributing to the formation of a Co-Fe alloy in the respective layers.

[0078] Next, the process for producing the spindle-shaped hematite particles according to the present invention is described below.

[0079] In the present invention, the surface of each spindle-shaped goethite particle is preferably preliminarily coated with an anti-sintering agent prior to heat-dehydration treatment thereof.

[0080] As the anti-sintering agent, there may be used rare earth compounds. Examples of the suitable rare earth compounds may include compounds of at least one element selected from the group consisting of scandium, yttrium, lanthanum, cerium, praseodymium, neodymium and samarium. The rare earth compounds may be in the form of chlorides, sulfates, nitrates or the like. The coating of the rare earth compound as anti-sintering agent may be conducted by either wet or dry method. Of these methods, the use of wet-coating method is preferred.

[0081] The amount of the rare earth compound used is preferably 1.5 to 5 atm%, more preferably 2.0 to 4.8 atm% (calculated as rare earth element) based on whole Fe.

[0082] By preliminarily coating the surface of each goethite particle with the anti-sintering agent, it is possible not only to inhibit the sintering of each particle and sintering between particles, but also to allow the spindle-shaped hematite particles to retain the particle shape and aspect ratio of the spindle-shaped goethite particles, thereby ensuring the production of individual spindle-shaped magnetic metal particles containing iron as a main component which can retain the shape and aspect ratio of the raw spindle-shaped goethite particles.

[0083] The spindle-shaped goethite particles surface-coated with the anti-sintering agent may be heat-treated at a temperature of usually 650 to 800°C in a non-reducing atmosphere. In this case, the heat-treatment is preferably conducted such that the ratio of crystallite size D_{104} of the obtained spindle-shaped hematite particles to crystallite size D_{110} of the spindle-shaped goethite particles [(crystallite size ratio of $D_{104}(\text{hematite})/D_{110}(\text{goethite})$)] is within the range of usually 1.0 to 1.3, preferably 1.1 to 1.3.

[0084] When the heat-treating temperature is less than 650°C, the crystallite size ratio of $D_{104}(\text{hematite})/D_{110}(\text{goethite})$ tends to become less than 1.0. As a result, the magnetic metal particles containing iron as a main component obtained from such spindle-shaped hematite particles tend to show a broad particle size distribution, so that the coating film produced therefrom tends to be deteriorated in SFD. When the heat-treating temperature is more than 800°C, the crystallite size ratio of $D_{104}(\text{hematite})/D_{110}(\text{goethite})$ tends to be more than 1.3. Therefore, the obtained hematite particles tend to suffer from shape breakage and sintering. As a result, the magnetic metal particles containing iron as a main component obtained from such hematite particles tend to show a broad particle size distribution and include sintered portions therein, and the magnetic coating film produced therefrom tends to be deteriorated in both squareness and SFD.

[0085] After the heat-treatment, the obtained hematite particles may be rinsed in order to remove impurity salts such as Na_2SO_4 therefrom. In this case, the rinsing is preferably conducted so as to remove only undesired impurity salts without elution of the anti-sintering agent coated. More specifically, the rinsing can be effectively performed under a high pH condition in order to remove cationic impurities, and under a low pH condition in order to remove anionic impurities.

[0086] Next, the spindle-shaped magnetic metal particles containing iron as a main component according to the present invention are described below.

[0087] The spindle-shaped magnetic metal particles containing iron as a main component according to the present invention contain Co in an amount of usually from 0.5 to less than 6 atm%, preferably from 0.5 to less than 5 atm% based on whole Fe; Al in an amount of usually from more than 10 to less than 20 atm%, preferably from 10.5 to 18 atm% based on whole Fe; a rare earth element in an amount of usually from 1.5 to 5 atm%, preferably from 2.0 to 4.8 atm% based on whole Fe, and have an atomic ratio of Al to Co of usually from more than 2 to 4, preferably from 2.10 to 3.90. The reason why the Al and Co contents of the spindle-shaped magnetic metal particles containing iron as a main component are defined to the above-specified ranges, are the same as those described as to the Al and Co contents of the spindle-shaped hematite particles.

[0088] The spindle-shaped magnetic metal particles containing iron as a main component according to the present invention have an average major axial diameter of usually 0.05 to 0.15 μm , preferably 0.06 to 0.15 μm ; a size distribution (standard deviation/average major axial diameter) of usually not more than 0.30, preferably 0.10 to 0.28; and an aspect ratio of usually 5:1 to 9:1, preferably 6:1 to 8:1.

[0089] When the average major axial diameter is less than 0.05 μm , the obtained magnetic metal particles containing iron as a main component have a too small particle size which is close to the particle size exhibiting a superparamagnetism, so that the saturation magnetization and coercive force as well as dispersibility in coating composition tend to be deteriorated, and the oxidation stability of the magnetic coating film obtained therefrom tends to be deteriorated.

When the average major axial diameter is more than 0.15 μm , it is difficult to obtain the aimed coercive force. In addition, since the particle size becomes too large, the obtained magnetic coating film tends to be deteriorated in surface smoothness, resulting in poor output characteristics thereof.

[0090] The spindle-shaped magnetic metal particles containing iron as a main component of the present invention preferably have a size distribution as small as possible. Although the lower limit of the size distribution is not particularly restricted, in the consideration of industrial productivity, the lower limit of the size distribution of the spindle-shaped magnetic metal particles containing iron as a main component is preferably about 0.10. When the size distribution is more than 0.30, the obtained particles tends to be deteriorated in oxidation stability, and the magnetic coating film obtained therefrom tends to be deteriorated in SFD, thereby failing to attain a high density recording performance thereof. When the aspect ratio is less than 5:1, there is a tendency that the spindle-shaped magnetic metal particles containing iron as a main component cannot show the aimed coercive force, and the magnetic coating film is deteriorated in both squareness and orientation ratio. When the aspect ratio is more than 9:1, the obtained particles tend to exhibit a too high coercive force or be deteriorated in oxidation stability.

[0091] The spindle-shaped magnetic metal particles containing iron as a main component according to the present invention have a crystallite size D_{110} of usually 130 to 160 \AA , preferably 135 to 155 \AA . When the crystallite size D_{110} is less than 130 \AA , although the noise of obtained magnetic recording media due to the particles is suitably reduced, the magnetic recording media are tend to be deteriorated in saturation magnetization and oxidation stability. When the crystallite size D_{110} is more than 160 \AA , the noise due to the particles is disadvantageously increased.

[0092] The spindle-shaped magnetic metal particles containing iron as a main component according to the present invention have a BET specific surface area of preferably 40 to 60 m^2/g , more preferably 45 to 60 m^2/g . When the BET specific surface area is less than 40 m^2/g , the obtained magnetic metal particles containing iron as a main component are already sintered together upon the previous heat-reduction treatment, so that it tends to be difficult to improve the squareness of the magnetic coating film obtained therefrom. When the BET specific surface area is more than 60 m^2/g , the viscosity of the obtained coating composition becomes too high to ensure a good dispersibility.

[0093] The spindle-shaped magnetic metal particles containing iron as a main component according to the present invention have a coercive force H_c of usually 111.4 to 143.2 kA/m (1,400 to 1,800 Oe), and a saturation magnetization σ_s of usually 110 to 160 Am^2/kg (110 to 160 emu/g).

[0094] The spindle-shaped magnetic metal particles containing iron as a main component according to the present invention have an oxidation stability of saturation magnetization ($\Delta\sigma_s$) of usually not more than 10%, preferably not more than 9% as an absolute value, and an ignition temperature of usually not less than 130°C, preferably not less than 135°C, after being subjected to an accelerated deterioration test at a temperature of 60°C and a relative humidity of 90% for one week.

[0095] As to properties of a coating film produced using the spindle-shaped magnetic metal particles containing iron as a main component according to the present invention, when the coating film is oriented by applying a magnetic field of 397.9 kA/m (5 kOe) thereto, the squareness (Br/Bm) thereof is preferably not less than 0.84, more preferably not less than 0.85; the orientation property (OR) thereof is preferably not less than 2.8, more preferably not less than 2.9; and the coercive force distribution (Switching Field Distribution: SFD) thereof is preferably not more than 0.53, more preferably not more than 0.52.

[0096] Also, when the coating film is oriented by applying a magnetic field of 238.7 kA/m (3 kOe) thereto, the squareness (Br/Bm) thereof is preferably not less than 0.82, more preferably not less than 0.83; the orientation property (OR) thereof is preferably not less than 2.6, more preferably not less than 2.7; and the coercive force distribution (SFD) thereof is preferably not more than 0.54, more preferably not more than 0.53.

[0097] The magnetic coating film produced using the spindle-shaped magnetic metal particles containing iron as a main component according to the present invention, have an oxidation stability (ΔBrm) of preferably not more than 8.0%, more preferably not more than 7.5% when the magnetic coating film is oriented by applying a magnetic field of 397.9 kA/m (5 kOe) thereto.

[0098] Next, the process for producing the spindle-shaped magnetic metal particles containing iron as a main component according to the present invention is described below.

[0099] In the present invention, the spindle-shaped magnetic metal particles containing iron as a main component are produced by heat-reducing the spindle-shaped hematite particles of the present invention. The heat-reducing temperature is preferably 400 to 700°C. When the heat-reducing temperature is less than 400°C, the reduction reaction proceeds too slowly and, therefore, requires a long period of time. When the heat-reducing temperature is more than 700°C, the reduction reaction proceeds too rapidly, so that deformation of particles and sintering within each particle or between particles tend to be caused.

[0100] The spindle-shaped magnetic metal particles containing iron as a main component which are obtained by the heat-reduction, may be taken out in air by known methods, for example, the method of immersing the particles in an organic solvent such as toluene; the method of replacing the atmosphere around the heat-reduced spindle-shaped magnetic metal particles containing iron as a main component, with an inert gas, and then gradually increasing the

oxygen content of the inert gas until the inert gas is completely replaced with air; and the method of gradually oxidizing the particles using a mixed gas of oxygen and water vapor.

[0101] Next, the magnetic recording medium according to the present invention will be described.

[0102] The magnetic recording medium according to the present invention comprises a non-magnetic substrate, and a magnetic recording layer which is formed on the non-magnetic substrate and comprising the magnetic metal particles containing iron as a main component and a binder resin.

[0103] As the non-magnetic substrate, there may be used those ordinarily used for magnetic recording media. Examples of the non-magnetic substrates may include films of synthetic resins such as polyethylene terephthalate, polyethylene, polypropylene, polycarbonates, polyethylene naphthalate, polyamides, polyamideimides and polyimides; foils or plates of metals such as aluminum and stainless steel; or various kinds of papers. The thickness of the non-magnetic substrate varies depending upon materials used, and is usually 1.0 to 300 μm , preferably 2.0 to 200 μm .

[0104] As the non-magnetic substrate for magnetic discs, there may be generally used a polyethylene terephthalate film having a thickness of usually 50 to 300 μm , preferably 60 to 200 μm . As the non-magnetic substrate for magnetic tapes, there may be used a polyethylene terephthalate film having a thickness of usually 3 to 100 μm , preferably 4 to 20 μm , a polyethylene naphthalate film having a thickness of usually 3 to 50 μm , preferably 4 to 20 μm , or a polyamide film having a thickness of usually 2 to 10 μm , preferably 3 to 7 μm .

[0105] As the binder resins, there may also be used those presently ordinarily used for the production of magnetic recording media. Examples of the binder resins may include vinyl chloride-vinyl acetate copolymer resins, urethane resins, vinyl chloride-vinyl acetate-maleic acid copolymer resins, urethane elastomers, butadiene-acrylonitrile copolymer resins, polyvinyl butyral, cellulose derivatives such as nitrocellulose, polyester resins, synthetic rubber-based resins such as polybutadiene, epoxy resins, polyamide resins, polyisocyanates, electron beam-curable acrylic urethane resins, or mixtures thereof.

[0106] The respective binder resins may contain a functional group such as $-\text{OH}$, $-\text{COOH}$, $-\text{SO}_3\text{M}$, $-\text{OPO}_2\text{M}_2$ and $-\text{NH}_2$ wherein M represents H, Na or K. In the consideration of the dispersibility of the magnetic metal particles containing iron as a main component in vehicle upon the production of a magnetic coating composition, the use of such binder resins containing $-\text{COOH}$ or $-\text{SO}_3\text{M}$ as a functional group is preferred.

[0107] The thickness of the magnetic recording layer formed on the non-magnetic substrate is usually 0.01 to 5.0 μm . If the thickness is less than 0.01 μm , uniform coating may be difficult, so that unfavorable phenomenon such as unevenness on the coating surface may be observed. On the contrary, when the thickness of the magnetic recording layer is more than 5.0 μm , it may be difficult to obtain desired electromagnetic performance due to an influence of diamagnetism. The thickness of the magnetic recording layer is preferably 0.05 to 4.0 μm .

[0108] The amount of the magnetic metal particles containing iron as a main component in the magnetic recording layer is usually 5 to 2,000 parts by weight, preferably 100 to 1,000 parts by weight based on 100 parts by weight of the binder resin.

[0109] When the amount of the magnetic metal particles containing iron as a main component is less than 5 parts by weight, the magnetic metal particles containing iron as a main component may not be continuously dispersed in a coating layer due to the too small content in a magnetic coating composition, resulting in insufficient surface smoothness and strength of the obtained coating layer. When the amount of the magnetic metal particles containing iron as a main component is more than 2,000 parts by weight, the magnetic metal particles containing iron as a main component may not be uniformly dispersed in the magnetic coating composition due to the too large content as compared to that of the binder resin. As a result, when such a magnetic coating composition is coated onto the substrate, it is difficult to obtain a coating film having a sufficient surface smoothness. Further, since the magnetic metal particles containing iron as a main component cannot be sufficiently bonded together by the binder resin, the obtained coating film becomes brittle.

[0110] The magnetic recording layer may further contain various additives used in ordinary magnetic recording media such as lubricants, abrasives and anti-static agents in an amount of 0.1 to 50 parts by weight based on 100 parts by weight of the binder resin.

[0111] The magnetic recording medium of the present invention has a coercive force value of usually 111.4 to 143.2 kA/m (1,400 to 1,800 Oe), and when the magnetic coating film is oriented by applying a magnetic field of 397.9 kA/m (5 kOe) thereto, a squareness (Br/Bm) of usually not less than 0.84, an orientation property (OR) of usually not less than 2.8, a coercive force distribution (Switching Field Distribution: SFD) of usually not more than 0.53 and an oxidation stability (ΔBm) of usually not more than 8.0%.

[0112] In the spindle-shaped goethite particles, the spindle-shaped hematite particles, the spindle-shaped magnetic metal particles containing iron as main component, and the processes for producing these respective particles, the point is that when the Co content, Al content and Al/Co ratio thereof are specified to the specified ranges, it is possible to obtain spindle-shaped magnetic metal particles containing iron as a main component which exhibit not only an adequate coercive force and good dispersibility and oxidation stability, but also an excellent coercive force distribution in spite of fine particles.

[0113] Conventionally, in order to obtain magnetic metal particles containing iron as a main component, which are excellent in magnetic properties and oxidation stability, it has been attempted to add various metals in the form of salts to the spindle-shaped goethite particles as a starting material. It is known that among these metals, Co forms a solid solution with iron in the obtained spindle-shaped magnetic metal particles containing iron as a main component, thereby enhancing the magnetization value and coercive force H_c thereof, and further improving the oxidation stability thereof. Therefore, it has been attempted to incorporate a large amount of cobalt into the magnetic metal particles in order to improve magnetic properties and oxidation stability thereof.

[0114] On the other hand, in the present invention, by specifying the Co and Al contents based on whole Fe, especially controlling the Al/Co ratio to the range of from more than 2 to 4, it becomes possible to obtain magnetic metal particles which exhibit an adequate coercive force and good dispersibility without deterioration of oxidation stability in spite of less Co content and fine particles. Meanwhile, the less amount of expensive Co added is also preferable from economical viewpoint.

[0115] In addition, in the present invention, when Co is added during aging step in the production reaction of the spindle-shaped goethite particles, the addition of Co is completed prior to the elapse of half a period of the whole aging time, and the oxidation reaction is controlled such that 40 to 50% of whole Fe is oxidized, so that the obtained goethite particles can exhibit a large minor axial diameter and a relatively small aspect ratio. Further, it has been found that when a magnetic coating film is prepared using the magnetic metal particles obtained by using the spindle-shaped goethite particles as a starting material, the squareness and orientation property of the obtained magnetic coating film can be remarkably enhanced.

[0116] The reason why the magnetic coating film having excellent squareness and orientation property can be produced in spite of using spindle-shaped goethite particles having a relatively small aspect ratio as starting material, is considered as follows. That is, by appropriately controlling the reaction conditions upon the addition of Co, the respective crystal planes (D_{020} , D_{110}) of goethite particles on which the surface layer has been formed, exhibit different crystal growth properties (crystallite sizes) from those of the goethite seed crystal particles, and the crystallite size ratio of D_{020}/D_{110} is adjusted to preferably 1.8 to 2.4. In addition to the above conditions, owing to the relatively small aspect ratio, an extremely excellent anti-sintering effect can be exhibited upon the heat-treatment and heat-reduction for the production of magnetic metal particles, so that the shape breakage of the particles can be effectively inhibited.

[0117] In the case where the ratio of the crystallite size D_{104} of the spindle-shaped hematite particles to the crystallite size D_{110} of the spindle-shaped goethite particles as a starting material [crystallite size ratio of D_{104} (hematite)/ D_{110} (goethite)] falls within the range of preferably 1.0 to 1.3 upon the heat-treatment prior to the heat reduction from the standpoint of improving the anti-sintering performance, it is possible to obtain the aimed spindle-shaped magnetic metal particles containing iron as a main component. Further, the magnetic coating film produced using such magnetic metal particles containing iron as a main component can show a high squareness, a high orientation property and a narrow coercive force distribution.

[0118] The reason why the magnetic coating film exhibiting a high squareness, a high orientation property and a narrow coercive force distribution can be obtained by defining the growth ratios of the specific crystal planes of the spindle-shaped goethite particles when converted into the spindle-shaped hematite particles, is considered as follows. That is, the obtained spindle-shaped hematite particles have a specific crystallite size ratio (D_{110}/D_{104} is preferably 2.0 to 4.0), and the crystallite size is adjusted such that the crystal growth of the spindle-shaped hematite particles can adequately control a reducing velocity thereof upon the heat-treatment. As a result, the sintering upon the reduction is effectively inhibited, and more than necessary growth, i.e., excessive growth beyond the size of the skeleton particle is appropriately prevented, so that the sintering and shape breakage upon the heat-treatment can be extremely reduced.

[0119] The spindle-shaped magnetic metal particles containing iron as a main component according to the present invention can exhibit an adequate coercive force, excellent oxidation stability, good dispersibility and excellent coercive force distribution notwithstanding the magnetic metal particles containing iron as a main component are fine particles, especially have an average major axial diameter as small as 0.05 to 0.18 μm and, therefore, suitable as magnetic particles for magnetic recording media.

[0120] Since the spindle-shaped magnetic metal particles containing iron as a main component according to the present invention are fine particles and exhibit good dispersibility and excellent coercive force distribution, the magnetic recording medium produced using the magnetic metal particles containing iron as a main component can show a high image quality and a high output characteristics and, therefore, are excellent in recording reliability.

EXAMPLES

[0121] The present invention is described in more detail by Examples and Comparative Examples, but the Examples are only illustrative and, therefore, not intended to limit the scope of the present invention thereto.

[0122] Various properties were measured by the following methods.

(1) The average major axial diameter, average minor axial diameter and aspect ratio of particles are respectively expressed by averages of values measured by an electron microscope. The size distribution of the particles is expressed by the value obtained by dividing the standard deviation measured simultaneously with the above values, by the average major axial diameter.

(2) The Co, Al and rare earth contents were measured using an inductively coupled high-frequency plasma atomic emission spectroscope (SPS-4000 Model, manufactured by Seiko Denshi Kogyo Co., Ltd.).

(3) The specific surface area of particles is expressed by the value measured by BET method using "Monosorb MS-11" (manufactured by Cantachrom Co., Ltd.).

(4) The crystallite size of particles is expressed by the thickness of the crystallite in the direction perpendicular to each crystal plane of the respective particles measured by X-ray diffraction method. The value was calculated based on the X-ray diffraction peak curve prepared with respect to the respective crystal planes by using the following Scherrer's formula:

$$\text{Crystallite size} = K\lambda/\beta\cos\theta$$

wherein β is a true half-width of the diffraction peak which was corrected with respect to the width of machine used (unit: radian); K is a Scherrer constant ($= 0.9$); λ is a wavelength of X-ray used (Cu $K\alpha$ -ray 0.1542 nm); and θ is a diffraction angle (corresponding to a diffraction peak of the respective crystal planes).

(5) The magnetic properties of magnetic metal particles were measured using a vibration sample magnetometer "VSM-3S-15" (manufactured by Toei Kogyo Co., Ltd.) by applying an external magnetic field of 795.8 kA/m (10 kOe) thereto.

(6) The ignition temperature of magnetic metal particles was measured using TG/DTA measuring device "SSC5100TG/DTA22" (manufactured by Seiko Denshi Inc.).

(7) The magnetic properties of the magnetic coating film were measured by the following method.

[0123] The respective components as shown below were charged into a 100cc polymer bottle, and then mixed and dispersed together for 8 hours using a paint shaker (manufactured by Reddevil Co., Ltd.), thereby preparing a magnetic coating composition. The thus prepared magnetic coating composition was coated on a 25 μm -thick polyethylene telephthalate film using an applicator to form a coating layer having a thickness of 50 μm thereon. The obtained coating film was then dried in respective magnetic fields of 3 kOe and 5 kOe, thereby obtaining a magnetic coating film. The thus obtained magnetic coating film was measured to determine magnetic properties thereof.

Coating composition

[0124]

3 mm ϕ steel balls	800 parts by weight
Spindle-shaped magnetic metal particles containing iron as a main component	100 parts by weight
Polyurethane resin having sodium sulfonate groups	20 parts by weight
Cyclohexanone	83.3 parts by weight
Methyl ethyl ketone	83.3 parts by weight
Toluene	83.3 parts by weight

[0125] (8) The oxidation stability ($\Delta\sigma_s$) of the saturation magnetization (σ_s) of magnetic particles, and the oxidation stability (ΔB_m) of saturation magnetic flux density (B_m) of the magnetic coating film were measured as follows.

[0126] The magnetic particles and the magnetic coating film were placed in a constant-temperature oven maintained at 60°C and a relative humidity of 90 %, and allowed to stand therein for one week to conduct an accelerated deterioration test. Thereafter, the particles and the magnetic coating film were measured to determine the saturation magnetization value and saturation magnetic flux density, respectively. The oxidation stability values $\Delta\sigma_s$ and ΔB_m were calculated by dividing the difference (absolute value) between the values σ_s measured before and after the one-week accelerated test, and the difference (absolute value) between the values B_m measured before and after the one-week accelerated test, by the values σ_s and B_m measured before the accelerated test, respectively.

Example 1:<Production of spindle-shaped goethite particles>

[0127] 30 liters of a mixed aqueous alkali solution containing sodium carbonate and sodium hydroxide in amounts of 25 mol and 19 mol, respectively (the concentration of sodium hydroxide is equivalent to 27.5 mol% (calculated as normality) based on mixed alkali) were charged into a bubble tower whose temperature was adjusted to 47°C while passing a nitrogen gas therethrough at a superficial velocity of 2.20 cm/s. Then, 20 liters of an aqueous ferrous sulfate solution containing 20 mol of Fe^{2+} (the concentration of the mixed aqueous alkali solution is 1.725 equivalents (calculated as normality) based on the ferrous sulfate) were charged into the bubble tower and the contents of the bubble tower were aged therein for one hour and 15 minutes. Thereafter, 4 liters of an aqueous cobalt sulfate solution containing 0.96 mol of Co^{2+} (equivalent to 4.8 atm% (calculated as Co) based on whole Fe) was added to the bubble tower and the contents of the bubble tower were further aged for 3 hours and 45 minutes (ratio of time required for Co addition to whole aging time: 25%). After aging, air was passed through the bubble tower at a superficial velocity of 2.30 cm/s to conduct the oxidation reaction until the oxidation percentage of Fe^{2+} reached 40 %, thereby producing goethite seed crystal particles.

[0128] The water suspension containing the goethite seed crystal particles and having a Fe^{2+} oxidation percentage of 40 %, was taken out from the bubble tower, rapidly washed with a diluted aqueous acetic acid solution, filtered and then washed with water. As a result of the composition analysis of the obtained goethite seed crystal particles, it was confirmed that the Fe content was 54.2% by weight and the Co content was 2.42% by weight, and the crystallite sizes D_{020} and D_{110} (seed crystal particles) were 186 Å and 101 Å, respectively.

[0129] Then, one liter of an aqueous aluminum sulfate solution containing 2.4 mol of Al^{3+} (equivalent to 12.0 atm% (calculated as Al) based on whole Fe) was added at a feed rate of not more than 3 ml/s to conduct the oxidation reaction, and the reaction mixture was washed with water using a filter press until the electric conductivity reached 60 $\mu\text{S}/\text{cm}$, thereby obtaining a press cake.

[0130] A part of the obtained press cake was dried and pulverized by ordinary methods, thereby obtaining spindle-shaped goethite particles. As shown in the transmission electron micrograph of Fig. 1, the obtained goethite particles were of a spindle shape, and had an average major axial diameter of 0.173 μm , a standard deviation σ of 0.0288 μm , a size distribution (standard deviation/average major axial diameter) of 0.166, an average minor axial diameter of 0.0234 μm , an aspect ratio of 7.4:1 and a BET specific surface area of 175.7 m^2/g . The obtained goethite particles contained no dendritic particles, and had as whole particles, a crystallite size D_{020} of 197 Å, a crystallite size D_{110} of 104 Å and a crystallite size ratio of D_{020}/D_{110} of 1.89. Further, as to the relationship between the whole particles and the seed crystal particles, the crystallite size ratio of $D_{020}(\text{whole particles})/D_{020}(\text{seed crystal particles})$ was 1.06, and the crystallite size ratio of $D_{110}(\text{whole particles})/D_{110}(\text{seed crystal particles})$ was 1.03.

[0131] Further, the obtained goethite particles comprised 51.5% by weight of Fe, 2.61% by weight of Co and 2.98% by weight of Al. From the comparison of these values with those of the goethite seed crystal particles, it was confirmed that the Co content of the seed crystal portion of each goethite particle was 4.2 atm% based on Fe contained in the seed crystal portion. Also, it was confirmed that the existence amount of Co (Co concentration) contained in the seed crystal portion of each goethite particle was 88 based on whole Co (Co concentration) contained in the goethite particle, assuming that the existence amount of the whole Co (Co concentration) based on whole Fe is 100, and the existence amount of Co (Co concentration) contained in the surface layer portion of each goethite particle was 108 based on whole Co (Co concentration) contained in the goethite particle, assuming that the existence amount of the whole Co (Co concentration) based on whole Fe is 100. Furthermore, it was confirmed that the Co and Al contents of whole goethite particles was 4.8 atm% and 12.0 atm%, respectively, based on whole Fe, and Al was contained only in the surface layer portion.

Example 2:<Production of spindle-shaped hematite particles>

[0132] The press cake containing 1,000 g (9.22 mol as Fe) of the spindle-shaped goethite particles obtained in Example 1 was sufficiently dispersed in 40 liters of water. Two liters of an aqueous neodymium nitrate solution containing 121.2 g of neodymium nitrate hexahydrate (equivalent to 3.0 atm% (calculated as Nd) based on whole Fe contained in the goethite particle) was added to the dispersion, and then stirred. Further, after a 25.0 wt% sodium carbonate aqueous solution as a precipitating agent was added so as to adjust the pH of the dispersion to 9.5, the dispersion was washed with water using a filter press. The obtained press cake was extrusion-molded using a compression molding machine equipped with a mold plate having an orifice diameter of 4 mm, and the resultant molded product was dried at 120°C, thereby obtaining a molded product containing goethite particles coated with the neodymium

compound.

[0133] The goethite particles obtained by pulverizing the molded product had a Co content of 4.8 atm% based on whole Fe; an Al content of 12.0 atm% based on whole Fe; a Nd content of 3.0 atm% based on whole Fe; and an atomic ratio of Al to Co of 2.50. In addition, it was confirmed that Al was present only in the intermediate layer portion of each goethite particle, and Nd was present only in the outermost layer portion thereof.

[0134] The spindle-shaped goethite particles coated with the neodymium compound were heat-dehydrated in air at 760°C to obtain spindle-shaped hematite particles having an outermost layer composed of the neodymium compound, such that the ratio of the crystallite size D_{104} of the obtained spindle-shaped hematite particles to the crystallite size D_{110} of the spindle-shaped goethite particles [(crystallite size ratio of $D_{104}(\text{hematite})/D_{110}(\text{goethite})$)] was in the range of 1.0 to 1.3.

[0135] As shown in the transmission electron micrograph of Fig. 2, the obtained spindle-shaped hematite particles were of a spindle shape, and had an average major axial diameter of 0.158 μm , a standard deviation σ of 0.0293 μm , a size distribution (standard deviation/average major axial diameter) of 0.185, an average minor axial diameter of 0.0205 μm , an aspect ratio of 7.7:1 and a BET specific surface area of 43.5 m^2/g . In addition, it was confirmed that the Co content of the hematite particles was 4.8 atm% based on whole Fe; the Al content thereof was 12.0 atm% based on whole Fe; the Nd content thereof was 3.0 atm% based on whole Fe; and the atomic ratio of Al to Co was 2.50. Further, the obtained spindle-shaped hematite particles had a crystallite size D_{104} of 127 Å and a crystallite size ratio of $D_{104}(\text{hematite})/D_{110}(\text{goethite})$ of 1.22; and a crystallite size D_{110} of 270 Å and a crystallite size ratio of $D_{110}(\text{hematite})/D_{104}(\text{hematite})$ of 2.13.

Example 3:

<Production of spindle-shaped magnetic metal particles containing iron as a main component>

[0136] 100 g of the obtained spindle-shaped hematite particles having the outermost layer composed of the neodymium compound were charged into a fixed bed reducing apparatus having an inner diameter of 72 mm. The spindle-shaped hematite particles were heat-reduced at 480°C by passing a hydrogen (H_2) gas through the reducing apparatus at a flow rate of 35 liter/minute. After the hydrogen gas was replaced with a nitrogen gas, the particles were cooled to 65°C, and then the oxygen partial pressure in the reducing apparatus was gradually increased by passing water vapor therethrough until the oxygen content therein reached the same content as in air, thereby forming a stable oxide film on the surface of each particle.

[0137] As shown in the transmission electron micrograph of Fig. 3, the obtained magnetic metal particles containing iron as a main component had an average major axial diameter of 0.122 μm , a standard deviation σ of 0.0324 μm , a size distribution (standard deviation/average major axial diameter) of 0.266, an average minor axial diameter of 0.0175 μm , an aspect ratio of 7.0:1, a BET specific surface area of 51.7 m^2/g and a crystallite size D_{110} of 145 Å. Further, the magnetic metal particles containing iron as a main component had a uniform particle size, and contained no dendritic particles. In addition, it was confirmed that the Co content of the magnetic metal particles containing iron as a main component was 4.8 atm% based on whole Fe; the Al content thereof was 12.0 atm% based on whole Fe; the Nd content thereof was 3.0 atm% based on whole Fe; and the atomic ratio of Al to Co was 2.50.

[0138] As to the magnetic properties of the spindle-shaped magnetic metal particles containing iron as a main component, the coercive force H_c thereof was 131.5 kA/m (1,653 Oe); the saturation magnetization value σ_s thereof was 130.0 Am²/kg (130.0 emu/g); the squareness (σ_r/σ_s) thereof was 0.487; the oxidation stability $\Delta\sigma_s$ of saturation magnetization thereof was 7.1 % as an absolute value (measured value: -7.1%); and the ignition temperature thereof was 135°C.

[0139] Further, as to sheet magnetic characteristics of the spindle-shaped magnetic metal particles containing iron as a main component, when the sheet was oriented in a magnetic field of 397.9 kA/m (5 kOe), the sheet coercive force H_c was 131.0 kA/m (1,646 Oe); the sheet squareness (Br/Bm) was 0.852; the sheet orientation property (OR) was 3.22; the sheet SFD was 0.489; and ΔBr was 5.4% as an absolute value (measured value: -5.4%). Also, when the sheet was oriented in a magnetic field of 238.7 kA/m (3 kOe), the sheet coercive force H_c was 1,639 Oe; the sheet squareness (Br/Bm) was 0.842; the sheet orientation property (OR) was 3.10; the sheet SFD was 0.498; and ΔBr was 5.6% as an absolute value (measured value: -5.6%).

Examples 4 to 7 and Comparative Examples 1 to 3:

<Production of spindle-shaped goethite particles>

[0140] The same procedure as defined in Example 1 was conducted except that production conditions of spindle-shaped goethite particles, i.e., production reaction conditions and growth reaction conditions of goethite seed crystal

particles, were varied as shown in Tables 1 and 2, thereby obtaining spindle-shaped goethite particles. Various properties of the obtained spindle-shaped goethite particles are shown in Table 3. Meanwhile, in Table 1, the alkali ratio was calculated from the following formula:

$$\text{Alkali ratio} = (1/2 \text{ alkali hydroxide}) / (\text{whole alkali})$$

wherein whole alkali is a sum of 1/2 alkali hydroxide and alkali carbonate.

[0141] In addition, the equivalent ratio in Table 1 was calculated from the following formula:

$$\text{Equivalent ratio} = (\text{whole alkali}) / (\text{Fe}^{2+})$$

wherein whole alkali is a sum of 1/2 alkali hydroxide and alkali carbonate.

Examples 8 to 11 and Comparative Examples 4 to 10:

<Production of spindle-shaped hematite particles>

[0142] The same procedure as defined in Example 2 was conducted except that the spindle-shaped goethite particles obtained in Examples 4 to 7 and Comparative Examples 1 to 3 were used, and kind and amount of the coating material used for the anti-sintering treatment, the heat-dehydrating temperature and the subsequent heat-treatment temperature were varied, thereby producing spindle-shaped hematite particles. Production conditions are shown in Table 4, and various properties of the obtained spindle-shaped hematite particles are shown in Table 5.

Examples 12 to 15 and Comparative Examples 11 to 17:

<Production of spindle-shaped magnetic metal particles>

[0143] The same procedure as defined in Example 3 was conducted except that the heat-reducing temperature was varied, thereby producing magnetic metal particles. Production conditions and various properties of the obtained spindle-shaped magnetic metal particles are shown in Tables 6 and 7, and various properties of the sheet produced using the spindle-shaped magnetic metal particles are shown in Table 8.

Example 16:

<Production of magnetic recording medium>

[0144] 100 parts by weight of the spindle-shaped magnetic metal particles obtained in Example 3, 10.0 parts by weight of a vinyl chloride-vinyl acetate copolymer resin (tradename: MR-110, produced by Nippon Zeon Co., Ltd.), 23.3 parts by weight of cyclohexanone, 10.0 parts by weight of methyl ethyl ketone, 1.0 part by weight of carbon black particles (produced by Mitsubishi Chemical Corp., average particle size: 26 nm; BET specific surface, area: 130 m²/g) and 7.0 parts by weight of alumina particles "AKP-30" (tradename, produced by Sumitomo Kagaku Co., Ltd., average particle size: 0.4 μm) were kneaded together for 20 minutes using a kneader. The obtained kneaded material was diluted by adding 79.6 parts by weight of toluene, 110.2 parts by weight of methyl ethyl ketone and 17.8 parts by weight of cyclohexanone thereto, and then the resultant mixture was mixed and dispersed for 3 hours by a sand grinder, thereby obtaining a dispersion.

[0145] The obtained dispersion was mixed with 33.3 parts by weight of a solution prepared by dissolving 10.0 parts by weight (solid content) of a polyurethane resin (tradename: E-900, produced by Takeda Yakuhin Kogyo Co., Ltd.) in a mixed solvent containing methyl ethyl ketone and toluene at a mixing ratio of 1:1, and the resultant mixture was mixed and dispersed for 30 minutes by a sand grinder. Thereafter, the obtained dispersion was passed through a filter having a mesh size of 1 μm. The obtained filter cake was mixed under stirring with 12.1 parts by weight of a solution prepared by dissolving 1.0 part by weight of myristic acid and 3.0 parts by weight of butyl stearate in a mixed solvent containing methyl ethyl ketone, toluene and cyclohexanone at a mixing ratio (weight) of 5:3:2, and with 15.2 parts by weight of a solution prepared by dissolving 5.0 parts by weight of trifunctional low molecular weight polyisocyanate (tradename: E-31, produced by Takeda Yakuhin Kogyo Co., Ltd.) in a mixed solvent containing methyl ethyl ketone, toluene and cyclohexanone at a mixing ratio (weight) of 5:3:2, thereby producing a magnetic coating composition.

[0146] The obtained magnetic coating composition contained the following components :

Spindle-shaped magnetic metal particles	100 weight parts
Vinyl chloride-vinyl acetate copolymer resin	10 weight parts
Polyurethane resin	10 weight parts
Alumina particles	7.0 weight parts
Carbon black fine particles	1.0 weight part
Myristic acid	1.0 weight part
Butyl stearate	3.0 weight parts
Trifunctional low molecular weight polyisocyanate	5.0 weight parts
Cyclohexanone	56.6 weight parts
Methyl ethyl ketone	141.5 weight parts
Toluene	85.4 weight parts

[0147] The obtained magnetic coating composition had a viscosity of 5,650 cP.

[0148] The thus obtained magnetic coating composition was passed through a filter having a mesh size of 1 μm . Thereafter, the magnetic coating composition was coated on a 12 μm -thick polyester base film using a slit coater having a gap width of 45 μm and then dried, thereby forming a magnetic layer on the base film. The surface of the obtained magnetic recording layer was calendered and smoothened by an ordinary method, and then the film was cut into a width of 1/2 inch (1.27 cm). The obtained tape was allowed to stand in a curing oven maintained at 60°C, for 24 hours to sufficiently cure the magnetic recording layer therein, thereby producing a magnetic tape. The obtained coating layer had a thickness of 3.5 μm .

[0149] With respect to magnetic properties of the obtained magnetic tape, the coercive force value thereof was 131.4 kA/m (1,651 Oe); the squareness (Br/Bm) thereof was 0.890; the sheet orientation property (OR) was 3.83; the sheet SFD was 0.441; and ΔBm was 4.2 % as an absolute value (measured value: -4.2 %).

Table 1

Examples and Comparative Examples	Production of goethite particles				
	Production reaction of goethite seed crystal particles				
	Mixed aqueous alkali solution				
	Aqueous alkali carbonate solution		Aqueous alkali hydroxide solution		Alkali ratio*: (mol%)
	Kind	Amount used (mol)	Kind	Amount used (mol)	
Example 4	Na ₂ CO ₃	25	NaOH	19	27.5
Example 5	Na ₂ CO ₃	25	NaOH	19	27.5
Example 6	Na ₂ CO ₃	25	NaOH	19	27.5
Example 7	Na ₂ CO ₃	25	NaOH	19	27.5
Comparative Example 1	Na ₂ CO ₃	25	NaOH	19	27.5
Comparative Example 2	Na ₂ CO ₃	25	NaOH	19	27.5
Comparative Example 3	Na ₂ CO ₃	25	NaOH	19	27.5

Note: *Alkali ratio = $(1/2 \cdot \text{alkali hydroxide}) / (\text{whole alkali})$
 wherein whole alkali is a sum of $1/2 \cdot \text{alkali hydroxide}$ and
 alkali carbonate

Table 1 (continued)

Examples and Comparative Examples	Production of goethite particles		
	Production reaction of goethite seed crystal particles		
	Aqueous ferrous salt solution		Equivalent ratio**
	Kind	Amount used (mol)	
Example 4	FeSO ₄	20	1.725
Example 5	FeSO ₄	20	1.725
Example 6	FeSO ₄	20	1.725
Example 7	FeSO ₄	20	1.725
Comparative Example 1	FeSO ₄	20	1.725
Comparative Example 2	FeSO ₄	20	1.725
Comparative Example 3	FeSO ₄	20	1.725

Note **Equivalent ratio = (whole alkali)/(Fe²⁺) wherein whole alkali is a sum of 1/2·alkali hydroxide and alkali carbonate

Table 1 (continued)

Examples and Comparative Examples	Production of goethite particles		
	Production reaction of goethite seed crystal particles		
	Aging		
	Temperature (°C)	Time (hr)	Superficial velocity of nitrogen passed (cm/s)
Example 4	46	5	2.30
Example 5	48	5	2.10
Example 6	44	5	2.30
Example 7	45	5	2.20
Comparative Example 1	47	5	2.20
Comparative Example 2	46	5	2.30
Comparative Example 3	47	5	2.20

Table 1 (continued)

Examples and Comparative Examples	Production of goethite particles			
	Production reaction of goethite seed crystal particles			
	Cobalt compound			
	Kind	Amount added (Co/Fe) (atom%)	Addition time after initiation of aging (hr)	(Co addition time) / (whole aging time) (%)
Example 4	CoSO ₄	3.5	1.50	30
Example 5	CoSO ₄	3.0	1.00	20
Example 6	CoSO ₄	4.5	2.25	45
Example 7	CoSO ₄	4.0	1.75	35
Comparative Example 1	CoSO ₄	4.5	3.00	60
Comparative Example 2	CoSO ₄	3.5	1.50	30
Comparative Example 3	CoSO ₄	4.5	1.25	25

Table 1 (continued)

Examples and Comparative Examples	Production of goethite particles	
	Production reaction of goethite seed crystal particles	
	Superficial velocity of air passed (cm/s)	Temperature (°C)
Example 4	2.40	46
Example 5	2.20	48
Example 6	2.60	44
Example 7	2.45	45
Comparative Example 1	2.40	47
Comparative Example 2	2.40	46
Comparative Example 3	2.40	47

Table 2

Examples and Comparative Examples	Production reaction of goethite particles			
	Growth reaction of seed crystal particles			
	Aluminum compound			Superficial velocity of air passed (cm/s)
	Kind	Amount added (Al/Fe) (atom%)	Addition time (oxidation percentage of Fe ²⁺) (%)	
Example 4	Aluminum sulfate	10.5	40	2.40
Example 5	Aluminum sulfate	11.0	40	2.20
Example 6	Aluminum sulfate	14.4	40	2.60
Example 7	Aluminum sulfate	12.0	40	2.45
Comparative Example 1	Aluminum sulfate	13.0	40	2.40
Comparative Example 2	Aluminum sulfate	5.0	40	2.40
Comparative Example 3	Aluminum sulfate	21.0	40	2.40

Table 3

Examples and Comparative Examples	Properties of goethite particles		
	Shape	Average major axial diameter (l) (μm)	Standard deviation (σ) (μm)
Example 4	Spindle- shaped	0.151	0.0239
Example 5	Spindle- shaped	0.179	0.0294
Example 6	Spindle- shaped	0.089	0.0134
Example 7	Spindle- shaped	0.132	0.0207
Comparative Example 1	Spindle- shaped	0.061	0.0090
Comparative Example 2	Spindle- shaped	0.149	0.0240
Comparative Example 3	Spindle- shaped	0.171	0.0356

Table 3 (continued)

Examples and Comparative Examples	Properties of goethite particles			
	Size distributio n (σ/l)	Average minor axial diameter (μm)	Aspect ratio	BET specific surface area (m^2/g)
Example 4	0.158	0.0213	7.1:1	179.8
Example 5	0.164	0.0208	8.6:1	161.8
Example 6	0.151	0.0144	6.2:1	187.4
Example 7	0.157	0.0194	6.8:1	169.2
Comparative Example 1	0.148	0.0127	4.8:1	202.9
Comparative Example 2	0.161	0.0204	7.3:1	163.4
Comparative Example 3	0.208	0.0241	7.1:1	205.6

Table 3 (continued)

Examples and Comparative Examples	Properties of goethite particles		
	Composition of whole particles		
	Co content (Co/Fe) (atom%)	Al content (Al/Fe) (atom%)	Al/Co (-)
Example 4	3.5	10.5	3.00
Example 5	3.0	11.0	3.67
Example 6	4.5	14.4	3.20
Example 7	4.0	12.0	3.00
Comparative Example 1	4.5	13.0	2.89
Comparative Example 2	3.5	5.0	1.43
Comparative Example 3	4.5	21.0	4.67

Table 3 (continued)

Examples and Comparative Examples	Properties of goethite particles			
	Crystallite size			
	Seed crystal particles		Whole particles	
	D ₀₂₀ (1) (Å)	D ₁₁₀ (1) (Å)	D ₀₂₀ (Å)	D ₁₁₀ (Å)
Example 4	180	97	195	101
Example 5	191	104	212	107
Example 6	170	92	188	96
Example 7	176	95	191	98
Comparative Example 1	160	82	165	93
Comparative Example 2	181	101	197	102
Comparative Example 3	188	102	195	102

Table 3 (continued)

Examples and Comparative Examples	Properties of goethite particles		
	Crystallite size		
	Crystallite size ratio		
	D_{020}/D_{110}	$D_{020}/D_{020}(1)$	$D_{110}/D_{110}(1)$
Example 4	1.93	1.08	1.04
Example 5	1.98	1.11	1.03
Example 6	1.96	1.11	1.04
Example 7	1.95	1.09	1.03
Comparative Example 1	1.77	1.03	1.13
Comparative Example 2	1.93	1.09	1.01
Comparative Example 3	1.91	1.04	1.00

Table 4

Examples and Comparative Examples	Production conditions of hematite particles		
	Goethite used	Anti-sintering treatment	
		Kind of rare earth compound	Amount added (Re/Fe) (atom%)
Example 8	Example 4	Neodymium nitrate	3.5
Example 9	Example 5	Yttrium nitrate	2.0
Example 10	Example 6	Yttrium nitrate	4.8
Example 11	Example 7	Neodymium nitrate	4.0
Comparative Example 4	Comparative Example 1	Yttrium nitrate	4.8
Comparative Example 5	Comparative Example 2	Neodymium nitrate	3.5
Comparative Example 6	Comparative Example 3	Neodymium nitrate	3.0
Comparative Example 7	Example 3	Neodymium nitrate	1.0
Comparative Example 8	Example 4	Yttrium nitrate	6.5
Comparative Example 9	Example 5	Neodymium nitrate	4.0
Comparative Example 10	Example 5	Neodymium nitrate	4.0

Table 4 (continued)

Examples and Comparative Examples	Production conditions of hematite particles	
	Heat-treatment	
	Heating temperature (°C)	Atmosphere
Example 8	750	Air
Example 9	740	Air
Example 10	680	Air
Example 11	710	Air
Comparative Example 4	680	Air
Comparative Example 5	750	Air
Comparative Example 6	750	Air
Comparative Example 7	730	Air
Comparative Example 8	740	Air
Comparative Example 9	330	Air
Comparative Example 10	850	Air

Table 5

Examples and Comparative Examples	Properties of hematite particles		
	Shape	Average major axial diameter (l) (μm)	Standard deviation (σ) (μm)
Example 8	Spindle-shaped	0.137	0.0240
Example 9	Spindle-shaped	0.165	0.0299
Example 10	Spindle-shaped	0.082	0.0135
Example 11	Spindle-shaped	0.120	0.0205
Comparative Example 4	Spindle-shaped	0.054	0.0098
Comparative Example 5	Spindle-shaped	0.133	0.0313
Comparative Example 6	Spindle-shaped	0.157	0.0316
Comparative Example 7	Spindle-shaped	0.133	0.0295
Comparative Example 8	Spindle-shaped	0.168	0.0296
Comparative Example 9	Spindle-shaped	0.122	0.0206
Comparative Example 10	Spindle-shaped	0.118	0.0269

Table 3 (continued)

Examples and Comparative Examples	Properties of hematite particles			
	size distributio n (σ/l)	Average minor axial diameter (μm)	Aspect ratio	BET specific surface area (m^2/g)
Example 8	0.175	0.0185	7.4:1	44.8
Example 9	0.181	0.0185	8.9:1	42.0
Example 10	0.165	0.0126	6.5:1	55.8
Example 11	0.171	0.0169	7.1:1	48.9
Comparative Example 4	0.181	0.0110	4.9:1	54.1
Comparative Example 5	0.235	0.0193	6.9:1	37.1
Comparative Example 6	0.201	0.0201	7.8:1	70.5
Comparative Example 7	0.222	0.0215	6.2:1	33.0
Comparative Example 8	0.176	0.0183	9.2:1	55.6
Comparative Example 9	0.169	0.0169	7.2:1	123.3
Comparative Example 10	0.228	0.0174	6.8:1	39.4

Table 5 (continued)

Examples and Comparative Examples	Properties of hematite particles			
	Composition of whole particles			
	Co content (Co/Fe) (atom%)	Al content (Al/Fe) (atom%)	Rare earth content (Re/Fe) (atom%)	Al/Co ratio
Example 8	3.5	10.5	3.5	3.00
Example 9	3.0	11.0	2.0	3.67
Example 10	4.5	14.4	4.8	3.20
Example 11	4.0	12.0	4.0	3.00
Comparative Example 4	4.5	13.0	4.8	2.89
Comparative Example 5	3.5	5.0	3.5	1.43
Comparative Example 6	4.5	21.0	3.0	4.67
Comparative Example 7	3.5	10.5	1.0	3.00
Comparative Example 8	3.0	11.0	6.5	3.67
Comparative Example 9	4.0	12.0	4.0	3.00
Comparative Example 10	4.0	12.0	4.0	3.00

Table 5 (continued)

Examples and Comparative Examples	Properties of hematite particles	
	Crystallite size	
	D ₁₀₄ (Å)	D ₁₁₀ (Å)
Example 8	125	275
Example 9	131	288
Example 10	118	263
Example 11	122	266
Comparative Example 4	116	229
Comparative Example 5	153	296
Comparative Example 6	110	215
Comparative Example 7	153	290
Comparative Example 8	116	230
Comparative Example 9	50	203
Comparative Example 10	154	295

Table 5 (continued)

Examples and Comparative Examples	Properties of hematite particles		
	Crystallite size ratio (D_{110}/D_{104})	Goethite crystallite ($D_{110}(g)$) (Å)	Crystallite size ratio of hematite to goethite ($D_{104}/D_{110}(g)$)
Example 8	2.20	101	1.24
Example 9	2.20	107	1.22
Example 10	2.23	96	1.23
Example 11	2.18	98	1.24
Comparative Example 4	1.97	93	1.25
Comparative Example 5	1.93	102	1.50
Comparative Example 6	1.95	102	1.08
Comparative Example 7	1.90	101	1.51
Comparative Example 8	1.98	107	1.08
Comparative Example 9	4.06	98	0.51
Comparative Example 10	1.92	98	1.57

Table 6

Examples and Comparative Examples	Heat-reduction	
	Kind of hematite	Reducing temperature (°C)
Example 12	Example 8	460
Example 13	Example 9	490
Example 14	Example 10	420
Example 15	Example 11	440
Comparative Example 11	Comparative Example 4	420
Comparative Example 12	Comparative Example 5	460
Comparative Example 13	Comparative Example 6	480
Comparative Example 14	Comparative Example 7	420
Comparative Example 15	Comparative Example 8	500
Comparative Example 16	Comparative Example 9	440
Comparative Example 17	Comparative Example 10	440

Table 6 (continued)

Examples and Comparative Examples	Properties of magnetic metal particles containing iron as main component		
	Average major axial diameter (l) (μm)	Standard deviation (σ) (μm)	Size distribution (σ/l)
Example 12	0.105	0.0267	0.254
Example 13	0.128	0.0339	0.265
Example 14	0.063	0.0150	0.238
Example 15	0.092	0.0224	0.243
Comparative Example 11	0.045	0.0100	0.252
Comparative Example 12	0.100	0.0328	0.328
Comparative Example 13	0.126	0.0383	0.304
Comparative Example 14	0.098	0.0309	0.315
Comparative Example 15	0.132	0.0366	0.277
Comparative Example 16	0.090	0.0277	0.308
Comparative Example 17	0.091	0.0274	0.301

Table 6 (continued)

Examples and Comparative Examples	Properties of magnetic metal particles containing iron as main component		
	Average minor axial diameter (μm)	Aspect ratio	BET specific surface area (m^2/g)
Example 12	0.0154	6.8:1	50.3
Example 13	0.0164	7.8:1	48.9
Example 14	0.0102	6.2:1	58.7
Example 15	0.0142	6.5:1	53.5
Comparative Example 11	0.0100	4.5:1	53.9
Comparative Example 12	0.0164	6.1:1	38.6
Comparative Example 13	0.0173	7.3:1	63.7
Comparative Example 14	0.0169	5.8:1	34.4
Comparative Example 15	0.0157	8.4:1	53.8
Comparative Example 16	0.0143	6.3:1	39.8
Comparative Example 17	0.0147	6.2:1	38.6

Table 6 (continued)

Examples and Comparative Examples	Properties of magnetic metal particles containing iron as main component		
	Crystallite size D_{110} (Å)	Co content (Co/Fe) (atom%)	Al content (Al/Fe) (atom%)
Example 12	143	3.5	10.5
Example 13	152	3.0	11.0
Example 14	135	4.5	14.4
Example 15	141	4.0	12.0
Comparative Example 11	129	4.5	13.0
Comparative Example 12	168	3.5	5.0
Comparative Example 13	127	4.5	21.0
Comparative Example 14	162	3.5	10.5
Comparative Example 15	129	3.0	11.0
Comparative Example 16	164	4.0	12.0
Comparative Example 17	161	4.0	12.0

Table 6 (continued)

Examples and Comparative Examples	Properties of magnetic metal particles containing iron as main component	
	Rare earth content (Re/Fe) (atom%)	Al/Co ratio
Example 12	3.5	3.00
Example 13	2.0	3.67
Example 14	4.8	3.20
Example 15	4.0	3.00
Comparative Example 11	4.8	2.89
Comparative Example 12	3.5	1.43
Comparative Example 13	3.0	4.67
Comparative Example 14	1.0	3.00
Comparative Example 15	6.5	3.67
Comparative Example 16	4.0	3.00
Comparative Example 17	4.0	3.00

Table 7

Examples and Comparative Examples	Properties of magnetic metal particles containing iron as main component			
	Coercive force (Hc)		Saturation magnetization (σ_s)	
	(kA/m)	(Oe)	(Am ² /kg)	(emu/g)
Example 12	137.0	1,721	128.6	128.6
Example 13	126.5	1,590	132.2	132.2
Example 14	143.1	1,798	129.0	129.0
Example 15	138.7	1,743	127.5	127.5
Comparative Example 11	145.6	1,830	123.5	123.5
Comparative Example 12	128.1	1,610	138.9	138.9
Comparative Example 13	122.5	1,540	122.0	122.0
Comparative Example 14	128.2	1,611	137.9	137.9
Comparative Example 15	130.5	1,640	126.1	126.1
Comparative Example 16	110.5	1,389	144.4	144.4
Comparative Example 17	113.6	1,428	139.8	139.8

Table 7 (continued)

Examples and Comparative Examples	Properties of magnetic metal particles containing iron as main component		
	Squareness (σ_r/σ_s)	Oxidation stability of saturation magnetization ($\Delta\sigma_s$) (%)	Ignition temperature (°C)
Example 12	0.490	6.9	137
Example 13	0.486	6.0	141
Example 14	0.494	6.5	139
Example 15	0.488	6.2	143
Comparative Example 11	0.483	11.2	122
Comparative Example 12	0.481	10.5	126
Comparative Example 13	0.488	11.0	124
Comparative Example 14	0.482	8.9	133
Comparative Example 15	0.489	10.2	127
Comparative Example 16	0.476	9.7	129
Comparative Example 17	0.478	8.9	131

Table 8

Examples and Comparative Examples	Properties of magnetic coating film (when oriented in a magnetic field of 5 kOe)		
	Coercive force (Hc)		Squareness (Br/Bm)
	(kA/m)	(Oe)	
Example 12	136.1	1,710	0.850
Example 13	124.9	1,570	0.854
Example 14	142.8	1,795	0.846
Example 15	138.1	1,736	0.848
Comparative Example 11	145.8	1,832	0.833
Comparative Example 12	126.5	1,590	0.838
Comparative Example 13	119.6	1,503	0.830
Comparative Example 14	124.8	1,568	0.833
Comparative Example 15	129.7	1,630	0.842
Comparative Example 16	108.3	1,361	0.824
Comparative Example 17	111.5	1,401	0.829

Table 8 (continued)

Examples and Comparative Examples	Properties of magnetic coating film (when oriented in a magnetic field of 5 kOe)		
	Orientation property (OR)	SFD	ΔB_m (%)
Example 12	3.18	0.496	5.3
Example 13	3.30	0.488	4.7
Example 14	2.99	0.492	5.1
Example 15	3.05	0.495	4.8
Comparative Example 11	2.77	0.537	9.2
Comparative Example 12	2.78	0.544	8.9
Comparative Example 13	2.65	0.567	9.1
Comparative Example 14	2.65	0.564	7.8
Comparative Example 15	3.01	0.521	9.5
Comparative Example 16	2.45	0.589	8.6
Comparative Example 17	2.52	0.571	7.8

Table 8 (continued)

Examples and Comparative Examples	Properties of magnetic coating film (when oriented in a magnetic field of 3 kOe)		
	Coercive force (Hc)		Squareness (Br/Bm)
	(kA/m)	(Oe)	
Example 12	135.6	1,704	0.841
Example 13	124.2	1,561	0.850
Example 14	142.3	1,788	0.832
Example 15	136.9	1,720	0.839
Comparative Example 11	143.3	1,801	0.816
Comparative Example 12	125.4	1,576	0.819
Comparative Example 13	118.5	1,489	0.814
Comparative Example 14	123.4	1,551	0.818
Comparative Example 15	128.3	1,612	0.824
Comparative Example 16	105.8	1,330	0.802
Comparative Example 17	110.2	1,385	0.810

Table 8 (continued)

Examples and Comparative Examples	Properties of magnetic coating film (when oriented in a magnetic field of 3 kOe)		
	Orientation property (OR)	SFD	ΔB_m (%)
Example 12	3.02	0.507	5.4
Example 13	3.22	0.496	4.9
Example 14	2.81	0.507	5.4
Example 15	2.99	0.509	5.1
Comparative Example 11	2.49	0.555	9.4
Comparative Example 12	2.52	0.567	9.3
Comparative Example 13	2.45	0.571	9.4
Comparative Example 14	2.46	0.565	8.1
Comparative Example 15	2.78	0.538	9.7
Comparative Example 16	2.11	0.602	8.9
Comparative Example 17	2.20	0.598	8.2

Claims

1. Spindle-shaped goethite particles which have an average major axial diameter of from 0.05 to 0.18 μm , an aspect ratio of more than 6:1 and less than 10:1 and a size distribution (standard deviation/average major axial diameter) of not more than 0.20; which contain not less than 0.5 and less than 6 atm% of Co based on the total amount of Fe, and more than 10 and less than 20 atm% of Al based on the total amount of Fe; and which have an atomic ratio of Al to Co of more than 2:1 and not more than 4:1.

2. Particles according to claim 1, which contain not less than 0.5 and less than 5 atm% of Co, based on the total amount of Fe, and from 10.5 to 18 atm% of Al based on the total amount of Fe and which have an atomic ratio of Al to Co of from 2.10:1 to 3.90:1.
- 5 3. Particles according to claim 1 or 2, which have a BET surface area of from 130 to 200 m²/g, a crystallite size D₀₂₀ of from 150 to 250 Å, a crystallite size D₁₁₀ of from 80 to 120 Å and a crystallite size ratio of D₀₂₀/D₁₁₀ of from 1.8:1 to 2.4:1.
- 10 4. Particles according to claim 1 or 2 which have a crystallite size D₀₂₀ of from 150 to 250 Å, a crystallite size D₁₁₀ of from 80 to 120 Å and a crystallite size ratio of D₀₂₀/D₁₁₀ of from 1.8:1 to 2.4:1.
- 15 5. Spindle-shaped hematite particles which have an average major axial diameter of from 0.05 to 0.17 µm, an aspect ratio of more than 6:1 and less than 10:1, a size distribution (standard deviation/average major axial diameter) of not more than 0.22 and a crystallite size D₁₀₄ of from 100 to 140 Å; which contain not less than 0.5 and less than 6 atm% of Co based on the total amount of Fe, more than 10 and less than 20 atm% of Al based on the total amount of Fe, and from 1.5 to 5 atm% of a rare earth element based on the total amount of Fe; and which have an atomic ratio of Al to Co of more than 2:1 and not more than to 4:1.
- 20 6. Particles according to claim 5, which contain not less than 0.5 and less than 5 atm% of Co based on the total amount of Fe, from 10.5 to 18 atm% of Al based on the total amount of Fe, and from 2.0 to 4.8 atm% of a rare earth element based on the total amount of Fe, and which have an atomic ratio of Al to Co of from 2.10:1 to 3.90:1.
- 25 7. Particles according to claim 5 or 6, which have a BET surface area of from 40 to 70 m²/g, a crystallite size D₁₁₀ of from 200 to 300 Å, and a crystallite size ratio D₁₁₀/D₁₀₄ of from 2.0:1 to 4.0:1.
- 30 8. Particles according to claim 5 or 6 which have a crystallite size D₁₁₀ of from 200 to 300 Å and a crystallite size ratio of D₁₁₀/D₁₀₄ of from 2.0:1 to 4.0:1.
- 35 9. Spindle-shaped magnetic metal particles which contain iron as a main component, which have an average major axial diameter of from 0.05 to 0.15 µm, an aspect ratio of from 5:1 to 9:1, a size distribution (standard deviation/average major axial diameter) of not more than 0.30 and a crystallite size D₁₁₀ of from 130 to 160 Å; which contain not less than 0.5 and less than 6 atm% of Co based on the total amount of Fe, more than 10 and less than 20 atm% of Al based on the total amount of Fe, and from 1.5 to 5 atm% of a rare earth element based on the total amount of Fe; and which have an atomic ratio of Al to Co of more than 2:1 and not more than 4:1, a coercive force of from 111.4 to 143.2 kA/m, an oxidation stability of saturation magnetization (Δos) of not more than 10%, and an ignition temperature of not less than 130°C.
- 40 10. Particles according to claim 9, which contain not less than 0.5 and less than 5 atm% of Co based on the total amount of Fe, from 10.5 to 18 atm% of Al based on the total amount of Fe, and from 2.0 to 4.8 atm% of a rare earth element based on the total amount of Fe, and which have an atomic ratio of Al to Co of from 2.10:1 to 3.90:1.
- 45 11. Particles according to claim 9 or 10, which have a BET surface area of from 40 to 60 m²/g.
- 50 12. A process for producing spindle-shaped goethite particles as defined in claim 1, which process comprises:
 - (a) aging a water suspension containing a ferrous-containing precipitate produced by reacting a mixed aqueous alkali solution comprising an aqueous alkali carbonate solution and an aqueous alkali hydroxide solution with an aqueous ferrous salt solution in a non-oxidative atmosphere;
 - (b) conducting an oxidation reaction of the water suspension by passing an oxygen-containing gas through the suspension to produce spindle-shaped goethite seed crystal particles, upon the production of the seed crystal particles, adding not less than 0.5 and less than 6 atm% of a Co compound, calculated as Co, based on the total amount of Fe, to the water suspension containing the ferrous-containing precipitate during aging thereof but prior to the elapse of half of the whole aging time before initiation of the oxidation reaction, wherein the oxidation reaction is conducted such that 40 to 50% of the total amount of Fe²⁺ is oxidized;
 - 55 (c) adding more than 10 and less than 20 atm% of an Al compound, calculated as Al, based on the total amount of Fe, to the water suspension containing both the ferrous-containing precipitate and the spindle-shaped goethite seed crystal particles; and
 - (d) passing an oxygen-containing gas through the resultant water suspension so as to conduct an oxidation

reaction thereof, thereby growing a goethite layer on the surface of each seed crystal particle.

13. A process for producing spindle-shaped hematite particles as defined in claim 5, which process comprises:

- 5 (a) treating spindle-shaped goethite particles obtained by a process according to claim 12 with an anti-sintering agent comprising from 1.5 to 5 atm% of a rare earth compound, calculated as a rare earth element, based on the total amount of Fe; and
(b) then heat-treating the spindle-shaped goethite particles at a temperature of from 650 to 800°C in a non-reducing atmosphere.

10 14. A process for producing spindle-shaped magnetic metal particles containing iron as a main component as defined in claim 9, which process comprises heat-reducing spindle-shaped hematite particles obtained by a process according to claim 11 at a temperature of from 400 to 700°C in a reducing atmosphere.

15 15. A magnetic recording medium, comprising:

- a non-magnetic substrate; and
- a magnetic recording layer which is provided on the non-magnetic substrate and which comprises a binder resin and spindle-shaped magnetic metal particles which contain iron as a main component according to any one of claims 9 to 11.

FIG.1



FIG.2

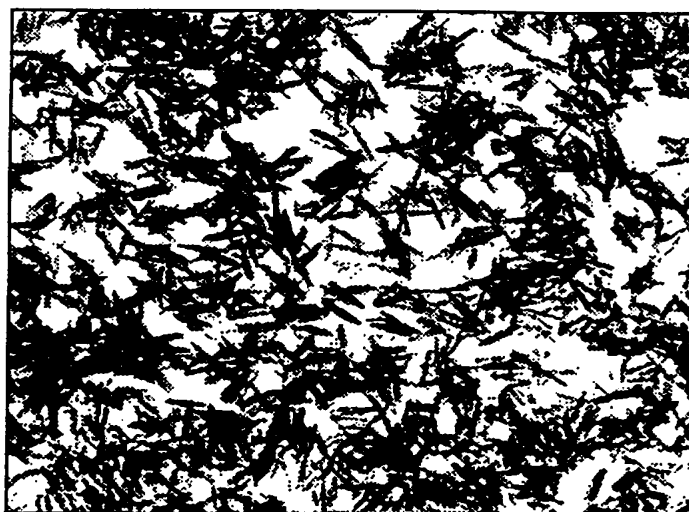


FIG.3



(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 164 581 A3

(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3:
20.03.2002 Bulletin 2002/12

(51) Int Cl.7: **G11B 5/706, C01G 49/06**

(43) Date of publication A2:
19.12.2001 Bulletin 2001/51

(21) Application number: **01305101.6**

(22) Date of filing: **12.06.2001**

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR**
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **13.06.2000 JP 2000177377**

(71) Applicant: **Toda Kogyo Corporation**
Hiroshima-shi, Hiroshima-ken (JP)

(72) Inventors:
• **Okinaka, Kenji**
Ube-shi, Yamaguchi-ken (JP)
• **Uegami, Masayuki**
Onoda-shi, Yamaguchi-ken (JP)

(74) Representative: **Woods, Geoffrey Corlett**
J.A. KEMP & CO.,
Gray's Inn,
14 South Square
London WC1R 5JJ (GB)

(54) **Spindle-shaped goethite particles, spindle-shaped hematite particles, spindle-shaped magnetic metal particles containing iron as main component and processes for producing the same**

(57) The present invention relates to spindle-shaped goethite particles which have an average major axial diameter of from 0.05 to 0.18 μm , an aspect ratio of more than 6:1 and less than 10:1 and a size distribution (standard deviation/average major axial diameter) of not more than 0.20; which contain not less than 0.5 and less than 6 atm% of Co based on the total amount

of Fe, and more than 10 and less than 20 atm% of Al based on the total amount of Fe; and which have an atomic ratio of Al to Co of more than 2:1 and not more than 4:1. The particles of the invention may be used in a magnetic recording layer of a magnetic recording medium.

EP 1 164 581 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 01 30 5101

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	EP 0 940 369 A (TODA KOGYO) 8 September 1999 (1999-09-08)	1,2, 12-14	G11B5/706 C01G49/06
Y	* page 2, line 54 - line 57 * * page 5, line 7 - page 6, line 20 * * page 7, line 18 - line 23 * * page 7, line 40 - page 8, line 39 *	3-11,15	
Y	DE 197 17 560 A (TODA KOGYO) 30 October 1997 (1997-10-30) * page 4, line 60 - page 5, line 11 * * page 6, line 20 - page 8, line 22 * * page 8, line 47 - line 52 * * page 10, line 6 - line 8 * * page 13, line 20 - line 23 * * page 15, line 30 - line 31 * * page 16, line 10 * * page 18, line 50 *	5-8	
Y	EP 0 125 150 A (KONISHIROKU) 14 November 1984 (1984-11-14) * page 2, line 10 - line 13 * * page 4, line 6 - line 12 * * page 20, line 8 - line 16 *	9-11,15	TECHNICAL FIELDS SEARCHED (Int.Cl.7) G11B
Y	EP 0 999 185 A (TODA KOGYO) 10 May 2000 (2000-05-10) * page 9, line 33 - line 45 * * page 10, line 22 - page 12, line 28 * * page 14, line 49 - line 52 * * page 14, line 56 - line 57 * * page 22, line 53 - line 58 *	3,4	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 23 January 2002	Examiner Magrizos, S
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPC FORM 15-3 (03/02) (F04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 01 30 5101

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

23-01-2002

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
EP 940369	A	08-09-1999	JP	11246224 A	14-09-1999
			EP	0940369 A2	08-09-1999
			US	2001051129 A1	13-12-2001
DE 19717560	A	30-10-1997	JP	3087825 B2	11-09-2000
			JP	9295814 A	18-11-1997
			DE	19717560 A1	30-10-1997
			US	6183868 B1	06-02-2001
			US	6048412 A	11-04-2000
EP 125150	A	14-11-1984	JP	1888172 C	07-12-1994
			JP	59207024 A	24-11-1984
			JP	63022366 B	11-05-1988
			DE	3484322 D1	02-05-1991
			EP	0125150 A2	14-11-1984
			US	4844977 A	04-07-1989
EP 999185	A	10-05-2000	EP	0999185 A1	10-05-2000
			JP	2000203847 A	25-07-2000
			US	6309479 B1	30-10-2001
			JP	2000226606 A	15-08-2000

EPO FORM P459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.